① **LEVEL Ⅱ**

THE APPLICATION OF ATOMIC ABSORPTION SPECTROSCOPY

AND OPTICAL MICROSCOPY TO THE CHARACTERIZATION OF

SIZED AIRBORNE PARTICULATE IN DAYTON, OHIO,

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science

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B.A. Rivier College, 1972

1978
Wright State University

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ABSTRACT

Krebs, Lorelei Ann. M.S., Department of Chemistry, Wright
State University, 1978. The Application of Atomic Absorp-
tion Spectroscopy and Optical Microscopy to the Characteri-
zation of Sized Airborne Particulate in Dayton, Ohio.

A four-stage Anderson cascade impactor, fitted onto
a standard high volume air sampler was used to collect 24-
hour suspended particulate samples at four sites in the Day-
ton, Ohio, metropolitan area. The particulate was impacted
on tared perforated aluminum foil disks and two sheets of
Whatman 41 cellulose paper were used as backup filters. The
suspended particulate was thus fractionated into five aero-
dynamic size ranges, each of which can be related to a
specific area of deposition within the human respiratory
tract. Some of the particles were removed from the collec-
tion media and mounted on slides with Aroclor 5662 for micro-
scopic examination. The foil impaction disks were cut into
eight sections each and the particles thereon dry ashed in
a low temperature asher for 30 minutes to remove any organic
materials. After ashing, each foil section was placed in
10 N nitric acid and the sample removed with a polyethylene
scraper. The scraper and foil were rinsed with distilled
water, and the total solution was slowly evaporated on a hot
plate to approximately 15 milliliters, then diluted in a 25
milliliter volumetric flask with distilled water. One-half

of each backup filter was cut into narrow strips, placed in
an aluminum foil boat and ashed for 16 hours. The result-
ing ash was dissolved in 10 N nitric acid and diluted with
distilled water in a 25 milliliter volumetric flask. Atomic
absorption spectroscopy was used to analyze the solutions
for chromium, iron, manganese, nickel, lead, and zinc.

The gravimetric data are presented by the convention-
al log-probability plots which give the probability of parti-
culate occurring below a specific aerodynamic diameter. The
mass median diameters (the diameter at 50% probability) at
all four sample sites were below 0.4 microns. The dispersion
of the sample about this mean, (standard deviation), varied
significantly between the industrial (4.7-10.7 microns) and
rural (30.1 microns) sites. Over sixty percent of the total
suspended particulate was below one micron in aerodynamic
diameter, a size easily retained by the lung.

The total elemental concentrations as determined by
atomic absorption are comparable to levels found in other
U. S. cities. Correlations are made between prevailing winds,
point sources and the sampling sites. Graphical display of
the percentage of elemental occurrence on the collection med-
ia reveals bimodal size distribution patterns for iron, man-
ganese, and zinc, with the largest percentage occurring on
the backup filters (less than 1.1 microns). Over 70% of the
lead at all sites is also associated with particles below
1.1 μ in aerodynamic diameter. The size distribution for
chromium is different at each site indicating very localized

point sources for the metal at each sampling site. Nickel was detected in nanogram amounts and only on the backup filters.

The particulate was examined microscopically and compared with grab samples from typical industrial point sources and representative soil samples from the Dayton area. Various biological and industrial materials were distinguished and characterized with photomicrographs.

It is concluded that an extensive elemental size distribution study of the Dayton metropolitan area would yield data critical to the identification of major pollution sources, lend additional insight into the potential hazards of toxic metals, and provide guidelines for the reevaluation of air quality regulations.

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ACKNOWLEDGMENTS

INTRODUCTION

Modern technology, spurred by federal regulation has almost completely transformed the industrial stacks of yesteryear from belchers of unsightly black smoke to more aesthetically pleasing, puffers of billowy, white clouds and spewers of virtually invisible emissions. However, increased concern is being focused on these visually benign stack emissions. The higher efficiencies of todays industrial boilers, together with the low efficiency of pollution abatement devices to control fine particulate, result in a serious health hazard which is only now being recognized. Present regulations[1] impose quantitative restrictions on suspended particulate matter, but do not address the problem of particle size as related to human inhalation, trace metal concentrations, or sorbed organics. Previous studies[2] have established that particles below 3 microns are retained by the human respiratory tract and can penetrate deep into the lung. It is also known that smaller particles remain airborne for longer periods of time and thus can travel far from their point source (Figure 1). Moreover, correlations of particle size data with elemental analysis reveal that the major fraction of toxic metals is found on particles within the respirable range,[3-5] and that

these toxic metals are on the surface of particles.[6-8]
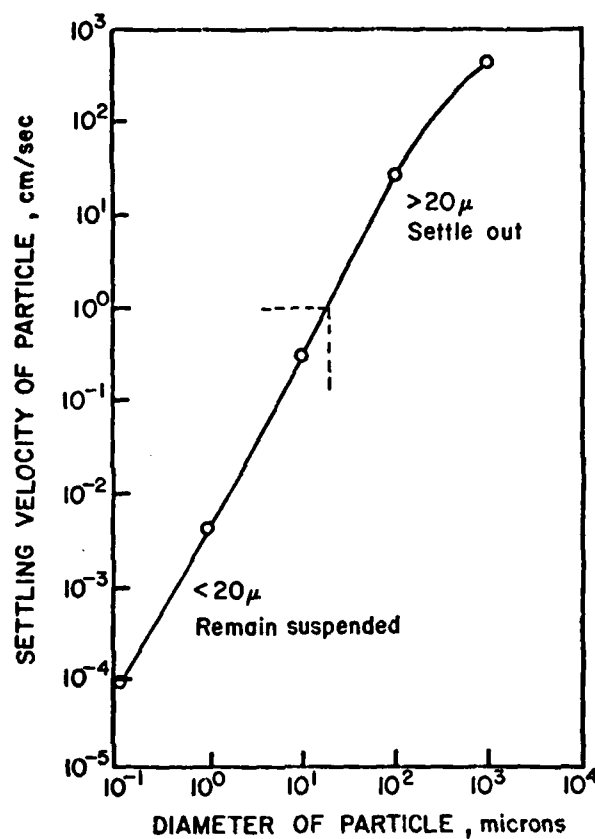
Figure 1. Settling Velocities in Still Air at 0°C
and 760 mm Pressure for Particles Having
a Density of 1 g/cm^3 as a Function of
Particle Diameter
(Ref: Stoker and Seager, 1976)

NEED FOR RESEARCH

As part of the National Air Surveillance Network, the
Regional Air Pollution Control Agency (RAPCA) monitors air
quality at 25 sites in a six-county area around Dayton, Ohio.
Suspended particulate matter is collected by a standard
high-volume sampler and concentration is gravimetrically
determined. Within recent years, many local industries
have installed pollution control equipment on their stacks
to lower particulate emissions; thus total particulate
levels have generally shown a decreasing trend. However,
the 1977 data revealed an unexpected reversal.[9] One third
of the monitoring sites recorded particulate levels higher
than those of the previous year. Fourteen sites exceeded
the Ohio suspended particulate standard and four of these
sites exceeded the federal primary standard (Appendices A
and B). In an attempt to determine the causes of nonattain-
ment, the Brehm Laboratory at Wright State University
received a grant from RAPCA, funded through the USEPA,
Region V, to characterize the various local industrial and
non-industrial sources, and relate this information to
elemental distributions on the high volume air filters.
Spark source mass spectroscopy and computer matching were
the primary analytical techniques used. This is the first
time an investigation of this type has been conducted in the
Dayton area.

Particle characterization studies have been made in
several major U.S. cities[11-13] (including Cincinnati[4] and

Cleveland[14,15]). The more definitive data has been the
result of correlating elemental occurrences with particle
size distributions. This entailed either optical sizing
methods after sample collection, or sizing during collection
using a fractionating sampler head. Since the samples for
the Brehm Laboratory study were collected with a high-volume
air sampler, and the filter medium (glass fiber) was not
entirely suited for microscopic examination of the partic-
ulate, no attempt was made to define the particle size
distribution. It was anticipated that an elemental size
distribution of the airborne particulate in Dayton would
yield further data critical to the identification of major
air pollution sources. A determination of toxic metals
within the respirable size range would also lend additional
insight into the potential hazards of this particulate and
provide guidelines for the reevaluation of air quality
regulations.

OBJECTIVE OF RESEARCH

The objective of this research is to chemically and
morphologically characterize sized airborne particulate in
the Dayton, Ohio metropolitan area. Samples were collected
with a multi-staged Anderson cascade impactor, at four sites
typifying both industrial and suburban atmospheres. Atomic
absorption spectroscopy was used to identify trace amounts
of Cr, Fe, Mn, Ni, Pb, and Zn. Size to weight distributions
were determined for the total collected particulate and the

indidivual elements. Visual comparisons between the
samples and particulate from known sources were documented
using photomicrography.

I. AIRBORNE PARTICULATE

DEFINITION AND OCCURRENCE

The term particulate is usually applied to any dispersed matter in which units of its condensed phase range from approximately 0.005 μ to 500 μ in diameter (Table 1). Throughout the literature, particulate and aerosol are used interchangeably. However, strictly speaking the term aerosol relates to particulate matter less than 1 μ in diameter which produces fairly stable dispersions, and is responsible for light scattering.[16] From the standpoint of air quality control, particulates may be classified as either primary or secondary pollutants.[17] Primary pollutants are those emitted directly into the atmosphere from anthropogenic or natural sources. These include flyash, dust, soot, pollen, and the like. They account for the major fraction of particles 1 μ and above. Secondary pollutants result from the chemical reactions of SO_2, NO_2, O_2, NH_3, H_2O, and hydrocarbons in the atmosphere and usually range from 0.01 to 1 μ in diameter. As seen by Table 2, natural emissions, primary and secondary, account for approximately 89% of the worldwide particulate emissions, while anthropogenic sources contribute the remaining 11%. Within the U.S., the major source of man-made pollution is due to industrial process losses (Table 3). This is followed by

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TABLE I

SIZE RANGES OF AIRBORNE PARTICULATES

FOUNDARY DUST					
PULVERIZED COAL					
SMOG					
H₂SO₄ MIST					
OIL SMOKE	HUMAN HAIR				
PIGMENTS					
CARBON BLACK	FLY ASH				
METALLURGICAL DUST and FUMES					
AUTO EXHAUST					
VIRUSES	PLANT SPORES				
AIKEN NUCLEI	COAL DUST				
COMBUSTION NUCLEI	INSECTICIDE DUSTS				
MOLECULES	BACTERIA	CEMENT DUST			
ZINC OXIDE FUMES	FOG	MIST			
SEA SALT NUCLEI	POLLENS				

0.001   0.01   0.1   1.0   10   100

MICRONS

(Ref. Stoker & Seager, 1972)
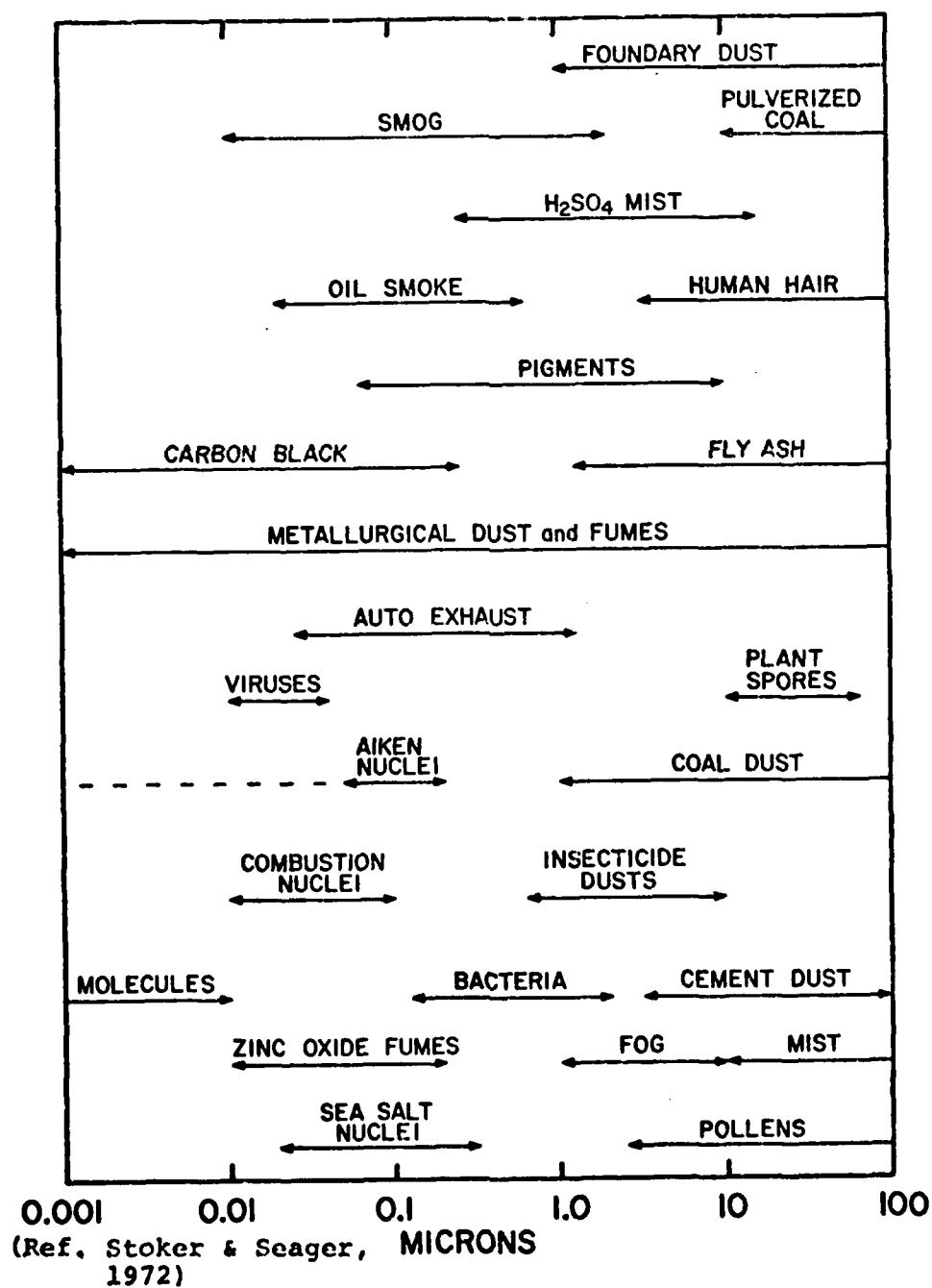
Table 2

GLOBAL PARTICULATE EMISSIONS FROM NATURAL
AND ANTHROPOGENIC SOURCES

Source	Production (millions of tons/year)
Anthropogenic	
pollutant particulate materials	92
particles formed from gaseous pollutants	
sulfate from SO_2	147
nitrate from NO_x	30
photochemical from hydrocarbons	27
Natural	
soil dust	200
particles from natural gaseous emissions	
sulfate from H_2S	204
nitrate from NO_x	432
ammonium from NH_3	269
photochemical from terpenes	200
volcanic (small particles)	4
forest fires	3
sea salt	1,000
TOTAL	2,608

(Ref: Robinson and Robbins, 1971)

Table 3

NATIONWIDE PARTICULATE EMISSIONS - 1970

Source	Emissions (millions of tons/year)			Percentage of Total		
Transportation	0.7			2.7		
motor vehicles		0.4			1.5	
gasoline			0.3			1.1
diesal			0.1			1.4
aircraft		0.1			0.4	
railroads		neg.			---	
vessels		0.1			0.4	
nonhighway use of fuels		0.1			0.4	
Fuel Combustion - stationary sources	6.8			26.1		
coal		5.6			21.5	
fuel		0.4			1.5	
natural gas		0.2			0.8	
wood		0.6			2.3	
Industrial Process Losses	13.3			51.0		
stone & rock crushing		4.2			16.1	
iron & steel		1.6			6.1	
grain handling		1.6			6.1	
cement		1.1			4.2	
lime		1.1			4.2	
pulp and paper		0.5			1.9	
asphalt batching		0.5			1.9	
feed mills		0.5			1.9	
copper		0.3			1.1	
other		1.9			7.3	
Solid Waste Disposal	1.4			5.4		
open burning		0.8			3.1	
on-site incineration		0.3			1.1	
other		0.3			1.1	
Miscellaneous	3.9			14.9		
agricultural burning		2.4			9.2	
forest fires		1.4			5.4	
other		0.1			0.4	
TOTAL	26.1					

(Ref: USEPA, AP-115, 1973)

stationary source fuel combustion, miscellaneous operations, solid waste disposal, and finally transportation. However, this information can be misleading without particle size distribution data.

PARTICLE SIZING

Unfortunately, although various studies have been made to characterize particulate by size, there is no standard sampling and analysis method. This makes it rather difficult to evaluate and compare the distribution data found in the literature. Particle size distributions can be based on number or weight.[18] A number distribution is compiled from physical or geometric diameters and is determined optically by microscopy or light scattering. This data can be useful when evaluating the efficiency of pollution control devices which operate primarily by filtration. Weight distributions are based on aerodynamically sizing the sample (impinger, cascade, cyclone), according to Stokes equivalent diameter, then weighing each sized fraction. The size to weight relationship yields a mass size distribution curve. This data can be directly related to particle retainability in the respiratory tract.[19]

In theory, using spherical particles of unit mass, number and mass distributions are equivalent. In practice however, this does not hold true. The majority of ambient particulate is irregular in shape and thus cannot be accurately sized optically. Light scattering techniques

also count water droplets and other volatile compounds which
are not determined gravimetrically.

SIZE DISTRIBUTION STUDIES

Particle size is probably the single most important
factor in determining the effects of suspended particulate
on man and his environment. In recent years, investigations
have shown relationships between source, elemental composi-
tion, and size. In fact, particle size distributions are
indispensible in determining emission sources and the
processes that control particle formation, dispersion, and
environmental impact. At the present time there are only
a few sources whose emissions have been fairly well char-
acterized. These are: marine aerosols,[11,13] lead and
halogen compounds from automotive exhaust gases,[20-23]
and to some extent, fly ash.[24-26] Extensive size data on
emissions from oil combustion, incineration[27] and most
other industries[4,28] is not readily available. It was once
assumed that characterization of raw materials would serve
to define elemental emission patterns. However, current
research indicates marked differences between the elemental
ratios of raw materials and stack emissions.[26,29-31]

Often times, the size distribution of particles con-
taining a given element provides the definitive clue
necessary to distinguish between different sources of the
element. For example, it is known that mechanical pro-
cesses such as wind erosion, grinding and pulverizing,
produce particles greater than 10 μ. Particles between

1 μ and 10 μ are often the result of process dusts and sea
salt (if applicable), while those between 0.1 μ and 1 μ are
primary combustion products and photochemical aerosols.
Combustion sources are also responsible for particulates
below 0.1 μ.

In a Toronto, Canada, study,[23] particle sizing was used
to distinguish between lead from automotive exhaust and
that emitted from a secondary lead refinery. At the urban
control sites, submicron lead, typical of auto emissions
was found.[20,32] In the vicinity of the refineries, however,
there was a definite increase in the lead concentration of
particles above 3.3 μ. In another study, thirteen elemental
constituents of fractionated aerosol collected in Miami,
Florida,[11] were classified according to particle size and
concentration. It was concluded that the larger size
fraction was due to soils and dusts, while the small,
respirable size fraction originated in combustion processes.
In Boston, Massachusetts[13] a cascade impactor was used to
collect atmospheric particulate at three sites. As expected
analysis for Na and Cl, Br, and V revealed distributions
typical of marine aerosols, auto emissions, and residential
oil combustion, respectively. Zinc, selenium, and antimony
were also found to occur as small particles indicating
origin in a combustion process. The larger particles, Al,
Sc, Fe, Th are thought to arise from fly ash, windblown soil,
and rock dust. Some elements, namely, Co, Mn, and Ce,
exhibited bimodal size distributions, possibly due to origin

in two or more processes of comparable magnitude.

Size distribution studies in conjunction with elemental analysis of airborne particulate as a means of identifying pollution sources have also been made in Cleveland[14,15] and Cincinnati, Ohio,[4] Tucson, Arizona,[33,34] Chicago, Illinois,[28] New York, New York,[35,36] and Palo Alto and Fresno, California.[37] The significant contributions of these investigations to the definition of air quality in their respective cities, suggests that a size distribution study of suspended particulate in Dayton, Ohio would also provide meaningful data for the determination of pollution sources and potential health hazards.

II. SAMPLING OF AIRBORNE PARTICULATE

THE HIGH-VOLUME AIR SAMPLER

The standard method for collecting airborne particulate in the U.S. and throughout much of the Western Hemisphere is the high-volume air sampler.[1] A relatively simple piece of equipment, it consists of a blower motor, face plate, gasket, and filter holder assembly. The unit is protected from debris and precipitation by a gable roofed aluminum shelter. It operates by drawing air through an 8 x 10 inch glass fiber filter at rates of 40 to 60 cfm. A calibrated rotameter is used to determine the rate of airflow. The glass fiber filter is nearly 100% efficient for particles of 0.3 μ or greater diameter.[38,39] Total suspended particulate (TSP) is computed from the mass loading on the filter and the total volume of air drawn through the filter during the sampling period.

High volume air sampling is not without sources of error. In practice, total air volume is determined from the average of the initial and final flow rates. Even though glass fiber filters exhibit a gradual buildup of resistance to air flow, and have excellent non-hygroscopic properties, the drop in air flow over a period of time may not always be linear, thus affecting the accuracy of the TSP calculation. This is especially true under conditions of high humidity

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or during collection of oily particulate. It is also desirable to maintain a constant sampling rate since it has been shown that filter efficiency is inversely proportional to air flow.[40] Cohen attributes this to the loss of sub-micron particles through reentrainment in a high velocity airstream. By using a hot wire anemometer to trigger a flow controller, constant airflow can be maintained.

Another possible source of error, discussed by Lee and Wagman,[41] is the formation of significant amounts of sulfate on the alkaline (pH 11) glass fiber filters due to the absorption of acid gases. This could pose a significant problem when sampling in an industrial environment. Adjusting the pH of the glass fiber filters to 6.5 eliminates the absorption of acid gases.[42]

Data obtained from the hi-vol sampler is of limited value and not highly accurate. As will be discussed later, glass fiber filters are not a suitable collection medium when particle characterization is desired, that is, when particle sizing; optical microscopy; or elemental analysis of the particulate is to be accomplished. Also, studies have shown reproducibility between concurrently operated samplers to be between 3.0 and 14%.[43,44]

Various other air samplers are available which allow further physical and chemical examination of the particulate. These include: cyclones; rotating centrifugal devices; cascade impactors, virtual impactors, and membrane filter samplers.[18,42,45-49]

THEORY OF CASCADE SAMPLER

Cascade impactors fractionate particulate according to aerodynamic size by taking advantage of the inertial forces of matter. When an obstacle is placed in the path of an airstream containing particulate, the airstream abruptly changes direction, while the particles, which do not follow the airstream, impact on a collection surface. This process was first theoretically described by May[49] and the treatment was refined by Rang and Wong.[50] They found that the impaction efficiency could be related to a dimensionless parameter, K, which they defined as:

$$\frac{CV_{p}d^2}{18\ nL} = K$$

C is the Cunningham slip factor which is equal to $1 + 0.08 \times 10^{-4}/d$. V is the air velocity across the impaction surface; d, the particle diameter; n the air viscosity; L, the jet width; and p the particle density. At the 50% effective cutoff diameter, the value of K for the cascade sampler used in this study is 0.14.[51] Since the efficiency of a cascade sampler varies continuously from 0 to 100% over a range of particle diameters and there is some overlap of the diameters collected on each stage, it is not possible to define a 100% effective cutoff diameter for any single stage. It has become accepted practice to define the effective cutoff diameter as the particle size at 50% collection efficiency.

In some cascade designs there is considerable overlap of particle size between stages. Also, the higher flow velocities required result in turbulence and reentrainment problems. The Anderson sampler uses approximately 300 small round jets which have been found to produce sharper cutoffs than a single large jet or rectangular jets.[50] Since each stage is multiorificed, the jet velocity is lower than on competitive models. This allows the collection plates to be closer to the jets thereby increasing the probability of particle impaction. Also reentrainment and turbulence are insignificant with this sampler. According to the operating manual collection of particulate in excess of 75 mg on any single stage is necessary before particle bounce becomes a problem.[51]

The Anderson cascade sampler used in this study is a four-staged, multi-orificed impactor designed to fit on a standard hi-vol air sampler. The unit contains five, 12.25 inch diameter aluminum plates ranging in thickness from 0.25 to 0.05 inches and containing approximately 300 precision-bore jets each. The plates, separated by neoprene gaskets, are stacked so that the orifices are offset from those of the preceding plate. Perforated disks of aluminum foil, glass fiber, or cellulose paper are used to collect the impacted sample. The entire sampling head is mounted over a glass fiber or cellulose paper filter on the hi-vol sampler, and is designed to operate at an air flow rate of 20 cfm (ref. Figures 2 and 3).

FIGURE 2

ANDERSON 2000 HIGH VOLUME PARTICLE SIZING SAMPLER

SPEEDBALL HANDLE

FLAT WASHER

SPECIAL WASHER

PLATE 1

COLLECTION DISC

PLATE 2

COLLECTION DISC

PROGRESSIVELY THINNER GASKETS

PLATE 3

COLLECTION DISC

PLATE 4

COLLECTION DISC

PLATE 5

THICKEST GASKET

INTERFACE PLATE
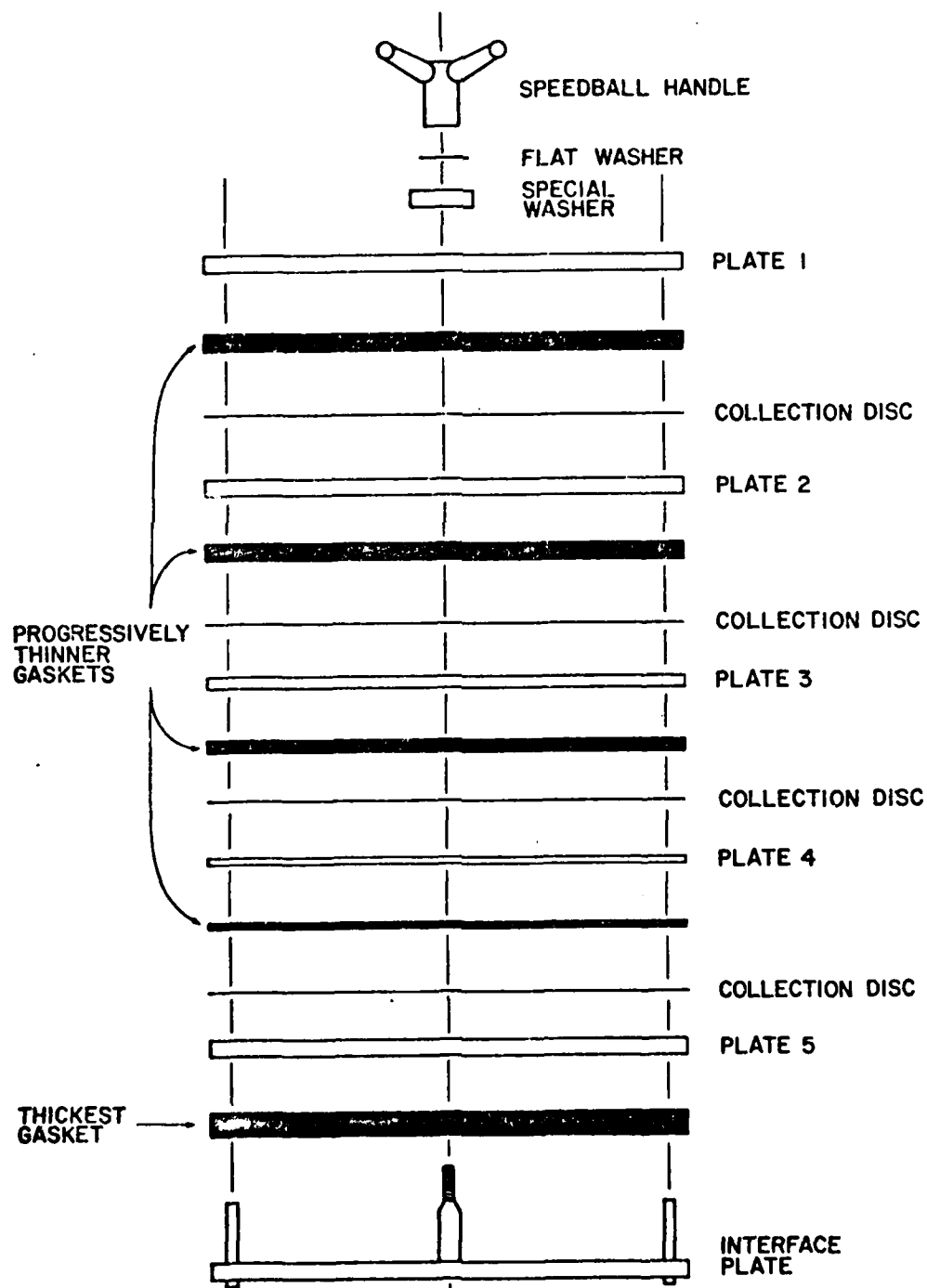
FIGURE 3

CROSS SECTION OF AIRFLOW THROUGH ANDERSON
2000 HIGH VOLUME PARTICLE   SIZING SAMPLER
(shown without gaskets)
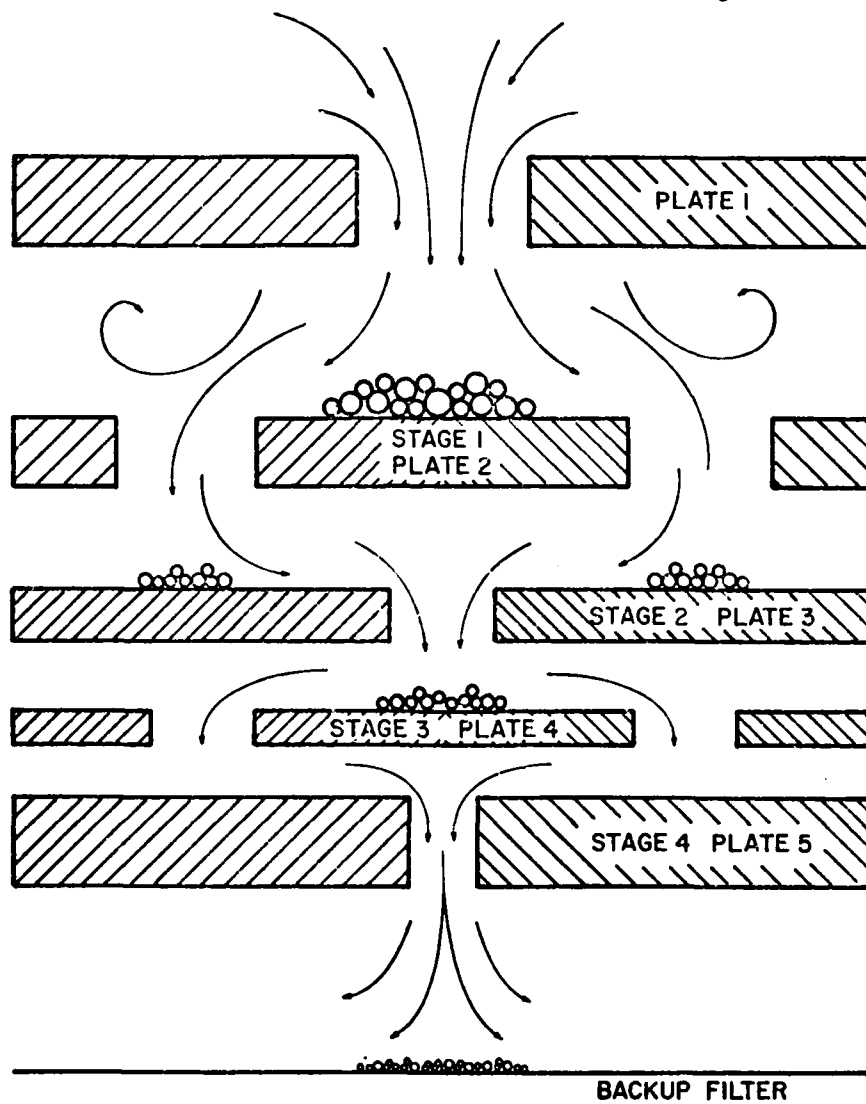
Each cascade sampler is supplied with a calibration
curve which relates pressure drop across the collection
plates with altitude. The correct flow rate is obtained
by reducing the voltage to the blower motor until the
desired pressure drop is reached (measured with an oil
manometer). The hi-vol samplers used in this study were
equipped with recording pressure transducers. Therefore,
it was possible to monitor flow rate throughout the sampling
period. Since the larger particles are collected by the
impactor, there is usually no problem with reduced air flow
due to sample buildup on the back-up filter.

The Anderson High Volume Fractionating Sampler was
designed to simulate the human respiratory tract which
aerodynamically sizes airborne particulate. The sampler
is calibrated with spherical particles of unit density thus
allowing one to equate the sampled particles to their equiv-
alent aerodynamic diameter. Figure 4 shows the relationship
between particle diameter and probable site of deposition
in the respiratory tract. Figure 5 shows the deposited
fraction of inhaled aerosols with respect to aerodynamic
diameter in a modelled respiratory tract. Table 4 lists
the mechanisms for particle deposition, the methods of
clearing the system, and the possible associated
pathologies.

The Anderson cascade sampler was clearly the fractionat-
ing particle collector of choice for this study. Its
superior multi-orificed design overcomes reentrainment and

Respiratory Tract	Impaction Stage	Effective Cutoff Diameter (microns)
nose	1	7.0 and up
larynx		
trachea		
primary bronchi	2	3.3-7.0
secondary bronchi	3	2.0-3.3
terminal bronchi	4	1.1-2.0
alveoli	backup filter	1.1 and below
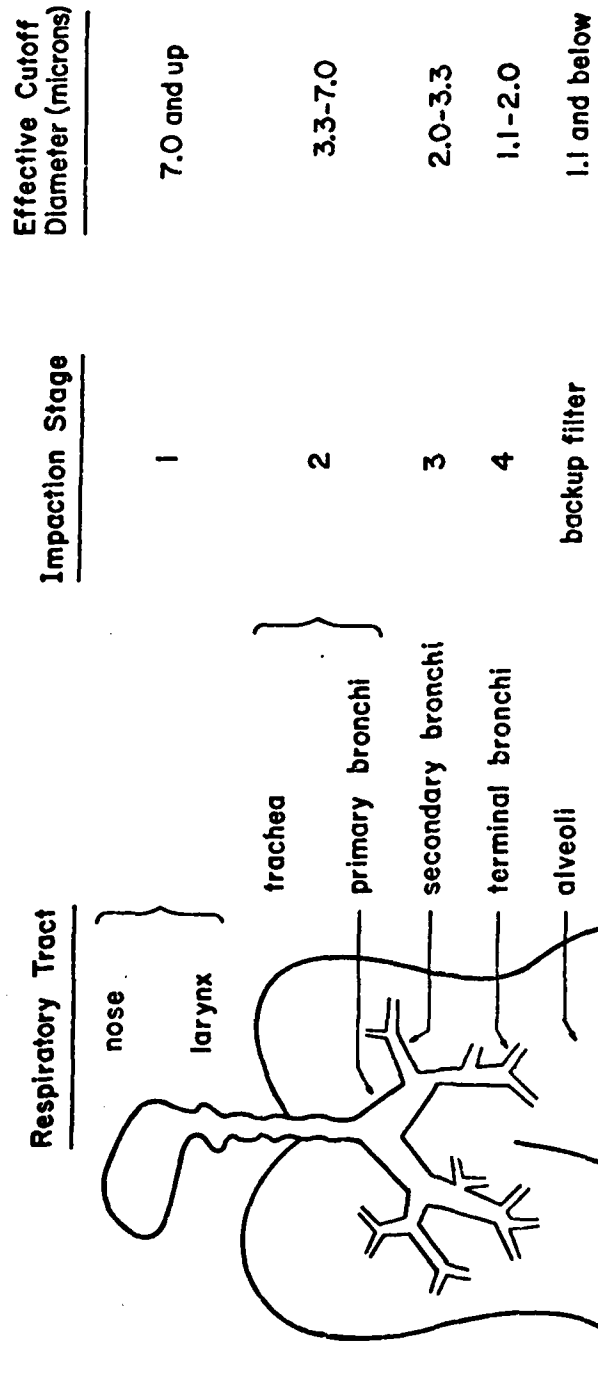
FIGURE 4   Effective cutoff diameter of impaction stages and relationship to deposition sites in human respiratory tract

(Ref. Anderson 2000 Inc., 1976)
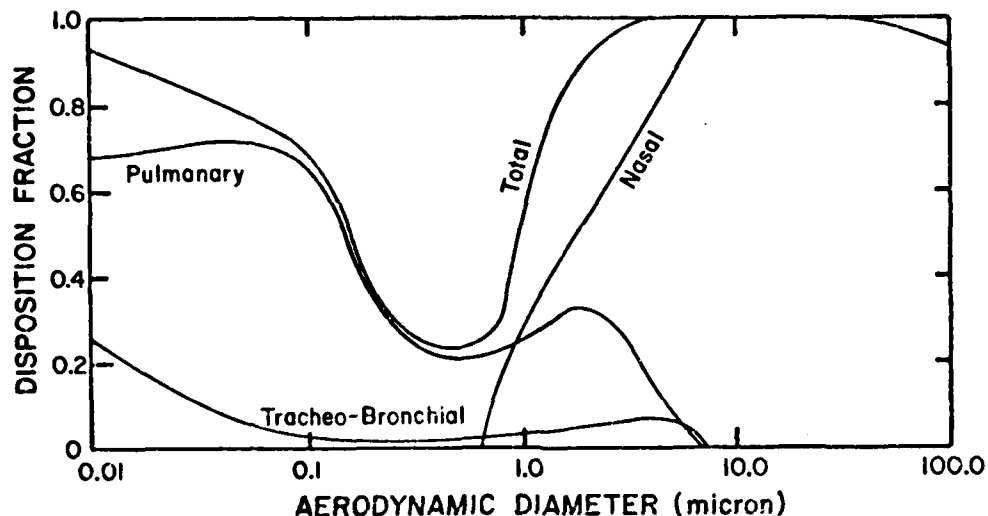
Figure 5. Deposition Fraction vs Aerodynamic
            Diameter

particles larger than 0.5 μ in physical diameter --
    motion governed by inertial and gravitational
    forces

particles below 0.5 μ in physical diameter --
    diffusional forces dominate; particles approach
    mean free path between collision of air molecules
    physical diameter correlates with aerodynamic
    size

particles at 0.5 μ in physical diameter -- minimum
    total deposition since particles are not
    influenced by either inertial or diffusional
    forces

(Ref: Task Group on Lung Dynamics, 1966; Phalen and
       Raabe, 1974)

Table 4

MECHANISMS OF PARTICULATE DEPOSITION IN THE
HUMAN RESPIRATORY TRACT

Respiratory Compartment	Mode of Deposition	Mechanisms of Clearance	Associated Pathology
Nasal Pharyngeal	impaction diffusion interception electrostatic	muco-ciliary (minutes) sneezing blowing	inflammation ulceration cancer
Tracheobronchial	impaction sedimentation diffusion interception	muco-ciliary (hours, longer?) coughing	broncho-spasm obstruction cancer
Parenchymal	sedimentation diffusion interception	solubilization phagocytosis interstitial (hours- years)	inflammation edema emphysema fibrosis cancer

(Ref: Task Group On Lung Dynamics, 1966).

to some extent particle shattering problems. Its ease
of operation and adaptibility to the standard hi-vol sampler
increased its desirability. There is minimum overlap
between aerodynamic particle size ranges and each fraction
can be related to a point of respiratory deposition. The
sampler also meets the design requirements of OSHA and EPA
for respirable/non-respirable fractionation.[51]

SELECTION OF SAMPLE COLLECTION MEDIA

There are two broad types of filters to consider,
fiber (cellulose, glass fiber), and membrane. Filters
serve to separate suspended particulate from air by sieving,
impaction and/or diffusion.[16,52,53] Sieving (membrane
filters primarily) is a mechanical operation whereby
particles larger than the pore size of the filter are
retained on the filter surface. Smaller particles may
become caught up within the membrane or pass completely
through it. The effective pore size of the filter decreases
as the particles build up on the membrane, thus arresting
the smaller particles at the surface also and rapidly
increasing flow resistance. When the moving stream of
particles is forced to flow around an obstruction (fibrous
network), or abruptly change direction, impaction occurs.
If the velocity is high enough, both large and small
particles are caught within the filter structure. The
principle collection mechanism for a low velocity stream of
air is diffusion, due to Brownian motion.

Filter Selection. There is no single universally acceptable filter. The best one can hope for is that the filter's useful characteristics outweigh its undesirable qualities. Selection should be guided by the type of sampler, the source to be sampled, and the analytical requirements. A desirable filter meets the following criteria: (1) at least 99% efficient in collecting particles greater than 0.3 μ; (2) absence of trace elements which might interfere with subsequent chemical analysis; and (3) low hygroscopcity.

Atmospheric samples are usually collected using either cellulose paper, glass fiber, or cellulose ester membrane filters. A summary of their properties is seen in Table 5. In the present study the backup filter was required between the cascade sampler and the hi-vol sampler. It was necessary for this filter to have a high collection efficiency for particles 1.1 μ and below, and to have a low resistance to flow. Since the filter was subjected to gravimetric analysis, hygroscopic characteristics were important. It was intended to use optical microscopy and atomic absorption spectroscopy as analytical methods to characterize the filters, thus dictating the need for a filter from which the sample could be easily removed. Therefore, an acceptable filter should also have a low ash content and low levels of trace elements. The medium of choice for gravimetric work is the glass fiber filter. However, there is reason to suspect the formation of sulfates

on the filter surface, which would lead to erroneous
calculation of suspended particulate.[41] Since the sample
becomes embedded within the glass fiber network it is
most difficult to perform microscopic analyses. Glass
fiber filters are also relatively high in trace elements.
Membrane filters are used when collecting a sample for
microscopic analysis. But, as seen from Table 5, they are
sensitive to moisture, have a high flow resistance, and
may contain elements which could interfere with instrumental
analyses. Cellulose paper filters are hygroscopic and
not entirely suited to microscopic analysis. However, they
have the lowest trace metal content and are easily ashed,
making them highly favorable for chemical analysis. In
consideration of the preceding, it was decided to use
Whatman 41 a cellulose paper filter.

Impaction Surface Selection. The cascade sampler
fractionates particles by impaction rather than filtration.
Once again, no single standard collection substrate is
recommended since the particulate characterization methods
dictate the type of impaction surface to be employed. In
a field evaluation of an Anderson cascade sampler, Burton
et al.[42] compared glass fiber and aluminum foil media.
Dams et al.,[54] looking for a surface suitable for non-
destructive neutron activation analysis, considered Teflon,
Mylar, and polyethylene. In a Miami[11] study, the fractionated
particles were collected by impaction on paraffin-coated,

ultrathin polystyrene film. Presumably, the paraffin would
provide an adhesive surface so as to negate the reen-
trainment problems encountered with some cascade designs.
It is also possible to collect the sample directly on
the impaction plates as was done in a study of the size
distribution of metal components in Cincinnati.[4] However,
this rules out the possibility of gravimetric analysis and
entails extracting the sample from the plates with HNO_3.

It has been shown that mass concentration values for
total suspended particulate collected by the Anderson
cascade impactor, using an aluminum foil substrate, are in
excellent agreement with those obtained with concurrently
run hi-vols.[42] Therefore, perforated aluminum foil disks
were used in this study. The particles could be readily
examined microscopically on the foil using reflected light.
The sample could also be removed for atomic absorption
measurements by simple agitation of the disks in an
extraction medium.

Table 5

PROPERTIES OF TYPICAL FILTER MEDIA RELATIVE TO VARIOUS TESTS IN ATMOSPHERIC ANALYSIS

Test Purpose	Cellulose Papers	Glass Fiber Paper	Membranes Cellulose Ester	Remarks
Mass loading gravimetric	X,1	2	3	1. Highly moisture-sensitive; low efficiency.
Mass loading dust spot	4	4	7	2. Good stability versus moisture; temperature resistant.
Mass loading light scatter	X,6	5	5,7	3. Moisture sensitive; high flow resistance.
Microscope count and size distribution	X	X	8,9	4. Paper usually in tape form.
Particle identity	X	X	8,9	5. Used to clean reference sample of air.
Chemical analysis wet methods	10	11	12	6. Low collection efficiency.
Chemical analysis instrumental	10	11	12	7. High flow resistance.
Biological assay	X	X	13	8. Good particle distribution on top surface.
Radiological	14	14	3,8,15	9. Select proper pore size.
Analysis for gaseous components	X	16	16	10. Use chemical grades and low ash if necessary.
				11. Interfering materials may extract from filter.

Table 5 (continued)

PROPERTIES OF TYPICAL FILTER MEDIA RELATIVE TO VARIOUS TESTS IN ATMOSPHERIC ANALYSIS

Test Purpose	Filter Type			Remarks
	Cellulose Papers	Glass Fiber Paper	Membrane Cellulose Ester	

Remarks:

12. Possibility of interfering materials in filter.

13. Standard filter for this use.

14. Not applicable α counts.

15. Suitable for all counts.

16. Danger of reaction or sorption versus gaseous components of air sample.

NOTE: Crosses indicate applicability unsuitable in most cases.

(Ref: Smith and Benson, 1974)

III. METHODS OF PARTICULATE ANALYSIS

In many studies, suspended particulate is collected
on glass fiber filters and non-destructive neutron
activation[13,54-56] or x-ray fluorescence[3,32,47] is used to
determine trace metals. The use of atomic absorption
(which was employed in the present study) however, requires
separation of the particulate from the filter. Dry ashing
of the glass fiber filter can lead to the formation of
insoluble metal silicates,[57] while the result of wet
ashing is often the loss of volatile metals and contamination
of the sample with small fragments of glass fiber. Kneip
et al.[12] and Scott et al.[58] report good recoveries using a
low temperature asher. In this study, the backup filters
were cellulose paper which can be dry ashed at temperatures
as high as 500°C without loss of trace metals if pretreated
with H_2SO_4.[57] For each of the stages of the cascade
sampler, an aluminum foil impaction medium was chosen due
to the ease of removing particulate from its surface for
analysis by atomic absorption. While atomic absorption
spectroscopy gives qualitative and quantitative data on the
identity and levels of selected elements in the particulate,
correlation of trace metal components with possible
pollution sources is difficult without the supplementary
aid of optical microscopy data on the particulates. With

25

proper equipment, particles above 0.2 μ can be reliably characterized using the light microscope, and usually a more definitive statement as to source can be made when this information is coupled with particulate chemical composition data.

OPTICAL MICROSCOPY

Optical microscopy is a powerful complement to particle characterization, especially in areas of environmental concern when one desires to ascertain the source of the contaminant. Light microscopy has been widely used to size airborne particulate and to identify its source. An extensive bibliography covering both the theory and applications of microscopy is found in The Particle Atlas.[59] This four volume atlas is the primary reference for microscopic examination of particulates whether it be light microscopy, transmission or scanning electron microscopy, electron microprobe analyzer, or ion microprobe analyzer. It was compiled by the world's foremost authority in particulate identification -- the Walter C. McCrone Laboratory.

ATOMIC ABSORPTION SPECTROSCOPY

Atomic absorption has been successfully used to analyze a wide range of metals in airborne particulate.[24,28,57,58,60] The technique is based on the theory that certain wavelengths emitted by excited atoms of a given element will be strongly absorbed by atoms of that same element which are in the ground state. The excited atoms are produced in a hollow

cathode discharge tube, and emit radiation characteristic of the particular element of which the cathode is made. The sample to be analyzed is aspirated into an air-acetylene flame and the spectrometer is tuned so that only the wavelength of choice can be absorbed by the ground state atoms in the flame. This absorption, which raises the sampled atoms to the excited state, is a direct measure of the number of atoms in the flame.

Atomic absorption measurements are subject to three types of interferences:[61] (1) matrix effects; (2) non-atomic absorption; and (3) chemical interferences. Matrix effects are the result of differences between the physical properties (viscosity, surface tension, density, solvent vapor pressure, etc.), of the standard and the sample, or due to precipitation of the analyte atom. These influence the amount of sample reaching the flame and can be corrected by preparation of the sample in a more appropriate medium and/or matching the physical properties of the standard and sample. Matrix effects can also be overcome using a standard addition technique.[62]

Non-atomic absorption is caused by molecular species which absorb in the same wavelength as the analyte element resonance line, and varies considerably with wavelength. Light scattering from high concentrations of total solids also contributes to non-atomic absorption. Sometimes a nearby line which is not absorbed by the element of interest can be used to measure the extent of the interference. One

can also circumvent the effect of molecular absorbance by subtracting out its absorbance as measured using a deuterium arc or hydrogen continuum lamp.[63]

Chemical interferences, which affect the number of atoms formed in the flame, are due to the formation of refractory compounds with, or ionization of, the element to be analyzed. The formation of refractory compounds which are not completely dissociated by the flame may be remedied by using a higher temperature flame; organic extraction of either the analyte element, or the interfering element; or by the addition of an excess of another element which will react with the interfering element. Ionization, observed with the alkali and alkaline earth metals, can be prevented by addition of a cation with a lower ionization potential than the analyte element.

In the present study atomic absorption was used to analyze for traces of lead, chromium, nickel, iron, manganese and zinc. There seems to be some question as to the need for matrix effect corrections in the analysis of lead in airborne particulate. In two studies by Burnham et al.,[64,65] the authors felt the particulate matrix to be unique and thus employed a standard addition technique.[62] However, in a more recent study,[58] excellent agreement between data obtained by atomic absorption and optical emission indicated that this was not necessary. While

the earlier measurements were obtained using the 217 nm resonance line, Scott et al.[58] chose instead the 283.3 nm line and did not experience problems of noise or baseline shift.

When working with wavelengths below 300 nm, as when analyzing for trace lead, molecular absorption and/or light scattering result in significant light losses. It was formerly widely accepted that light scattering played the major role. But Koirtyohann and Pickett[69-71] have shown molecular absorption to be more significant than previously believed.

Chromium analysis is affected by a variety of cationic interferences.[72] The presence of Co, Fe, and Ni, especially in perchloric acid, can depress the absorption curve for Cr(IV), while Ba, Ca, Al, Mg and Cu have an enhancing effect. The interferences are complex and depend heavily on burner height and flame stoichiometry.

Neither nickel nor zinc are subject to interferences. The manganese absorption curve is depressed by phosphate, perchlorate, Fe, Ni, and Co in a reducing flame. When using the 232 nm wavelength for nickel, non-atomic absorption can be a problem. But it is compensated for by using the 231.7 nm nickel non-absorbing line to measure the extent of interference.

IV. OBTAINING THE SAMPLE

EQUIPMENT

Particulate samples obtained in this study were collected using an Anderson 2000 High Volume Particle Sizing Sampler, serial #803 (Anderson 2000 Inc., P.O. Box 20769, Atlanta, Georgia 30320). This cascade sampling head was mounted on a hi-vol sampler. Airborne particulate was impacted on aluminum foil disks (supplied by Anderson 2000 Inc.) and two cellulose paper filters (Whatman 41, 8 x 10 in.) were used as backup filters to collect those particles 1.1 μ and below. The airflow through the sampler was adjusted to 20 cubic feet per minute (cfm). This was accomplished by reducing the line voltage to the blower motor with 120 VAC, 6.5 amp variac. Samples were collected over a 24-hr period (from midnight to midnight) and airflow was continuously monitored by a recording pressure transducer.

SITE SELECTION

All samples were obtained at established air quality monitoring sites maintained by the Regional Air Pollution Control Agency (RAPCA). With the advice of RAPCA Technical Services Personnel, four sites were selected which would yield particulate typical of suburban and industrial atmospheres. These sites, their location, and the weather conditions during the sampling period are given in Table 6.

Figure 6 shows the location of each sampling site with respect to potential particulate sources , while Table 7 lists some of the typical industrial sources in the RAPCA monitoring area. No map is provided for the New Carlisle site (#613) since it is not located near any significant suspended particulate sources.

Table 6

SAMPLING SITES AND SIGNIFICANT WEATHER

RAPCA Site No.	Sample ID No.	Location	Sampling Dates	Significant Winds and Weather
2	1	214 Valley Street Dayton	13-14 Sept 1978	12 mdnite-7 am SW-S 5 kts 7 am-10 am S-SE 9 kts 10 pm-12 mdnite S-SW-NW 10-14 kts foggy, hazy, rain
29	2	317 Abbey Street Dayton	18-19 Sept 1978	12 mdnite-7 am S-SW 8-12 kts 7 pm-12 mdnite SW-W foggy, hazy, clear by 11 am
613	3	432 N. Main Street New Carlisle	20-21 Sept 1978	12 mdnite-10 am SW-W 5-10 kts 10 am-3 pm S-SW-W 5-10 kts 3 pm-12 mdnite NW 13-15 kts frontal passage
8	4	2728 Viking Lane Moraine	3-4 Oct 1978	12 mdnite-8 am N-E 4 kts 8 am-6 pm SE-S-SE 5-10 kts 6 pm-12 mdnite SW 10-13 kts rain in evening
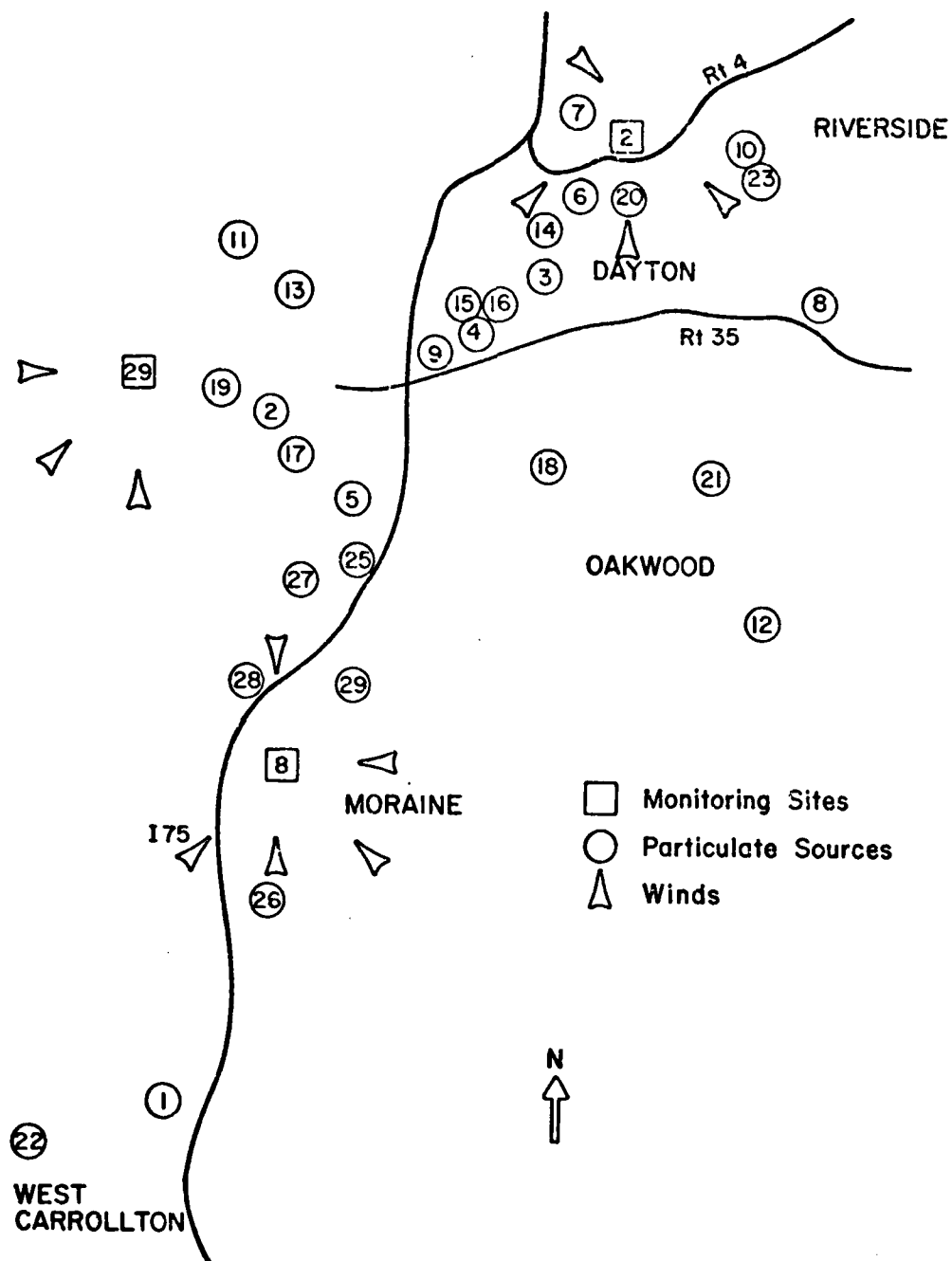
FIGURE 6

Monitoring sites in relation to particle sources in the
Dayton metropolitian area

Table 7

TYPICAL PARTICULATE SOURCES IN
THE RAPCA MONITORING AREA

No.	Name	Location	Number of Particulate Source
1.	Bergstrom Paper Co.	W. Alex-Bell Rd.	1 coal fired boiler
2.	NIBCO-Dayton	1800 McCall St.	gray iron foundry, 7 sources
3.	DP&L	Third Street	coal fired boilers
4.	DP&L	Longworth Steam Station	4 coal fired boilers
5.	Delco Moraine Div. GMC	1420 Wisconsin Blvd.	2 coal fired boilers
6.	GHR Foundry Div. DMI	400 Detrick St.	gray iron foundry, 19 sources
7.	Dayton Casting Co.	300 Kiser St.	2 sources
8.	Advance Foundry	107 Seminary Ave.	3 sources
9.	Howard Paper Mill	115 Columbia Street	2 coal fired boilers 1 source
10.	Valley Asphalt	3322 Stanley Ave.	3 sources
11.	Dayton Tire & Rubber Co.	2342 W. Riverview Ave.	4 sources
12.	DESC	1507 Wilmington Pike	4 coal fired boilers
13.	Republic Asphalt Paving Co.	N. Summit St. at Penn RR	2 sources
14.	Delco Products, Div. GMC	329 E. First St.	1 source
15.	Miami Valley Milk Producers Assn.	135 S. Perry St.	1 source

Table 7 (continued)

TYPICAL PARTICULATE SOURCES IN
THE RAPCA MONITORING AREA

No.	Name	Location	Number of Particulate Source
16.	United Color Press	240 W. Fifth St.	1 source
17.	Dayton Walther Corp.	1366 Miami Chapel	steel foundry 4 sources
18.	NCR	S. Main & K Sts.	4 sources
19.	Inland, Div. GMC	2727 Inland Ave.	3 coal fired boilers 3 sources
20.	City of Dayton Lime Plant	1044 Ottawa St.	2 sources
21.	Dayton Mental Health Center	2335 Wayne Ave.	2 coal fired boilers
22.	DP&L	Hutchings Station 9200 Chautauqua Rd.	6 coal fired boilers
23.	Duriron Co.	450 N. Findlay St.	gray iron foundry, 19 sources
24.	Miami Foundry Corp.	6th St. & Kercher St.	gray iron foundry, 2 sources
25.	DP&L	Tait Station E. River & Dryden Rd.	2 coal fired boilers, 4 oil fired boilers
26.	Delco Air Conditioning, Div. GMC	Springboro Pike	6 coal fired boilers 1 source
27.	Valley Asphalt	1901 Springboro	1 source
28.	NDM Corp.	3040 E. River Rd.	1 source
29.	Montgomery County South Reduction Plant	2550 Bertwynn Dr.	2 sources

V. EXPERIMENTAL PROCEDURES AND DATA

GRAVIMETRIC ANALYSIS

The aluminum foil impaction disks and cellulose paper backup filters were desiccated for at least 24 hours and tared on an analytical balance both before and after sample collection. Corrections for changes in temperature and humidity were determined from the weight change of blank collection media tared at the same time as the sampling media. A tabulation of net weight for collected particulate, the percent weight on each stage, and the cumulative percent less than the stated effective cutoff diameter (ECD) is given in Table 8. Plots on log-probability paper of the particle size versus cumulative percent less than ECD are given for each site sampled (Figures 7-10). The curves are extrapolated through the fifty percent point to yield the mass median diameter of the particulate (MMD). The particle size standard deviation (σ_g) is an indication of the size dispersion of the sample. For a log normal distribution, σ_g is calculated by either equation (1) or (2).

$$\sigma_g = \frac{84.13\% \text{ diameter}}{50\% \text{ diameter}} \tag{1}$$

$$\sigma_g = \frac{50\% \text{ diameter}}{15.87\% \text{ diameter}} \tag{2}$$

Table 8

GRAVIMETRIC RESULTS OF AIRBORNE PARTICULATE SAMPLED IN
DAYTON, OHIO WITH A CASCADE IMPACTOR

Impactor Stage	Net Wt (mg)	%	Cum. % Less Than	ECD (microns)
		Site #2		
1	22.5	10.15	89.85	7.0
2	18.9	8.53	81.32	3.3
3	16.0	7.22	74.10	2.0
4	11.2	5.05	69.05	1.1
filter	153.1	69.05		
	221.7			
		Site #29		
1	5.5	3.00	97.00	7.0
2	9.4	5.11	91.89	3.3
3	10.6	5.79	86.10	2.0
4	19.4	10.56	75.54	1.1
filter	138.7	75.54		
	183.6			
		Site #613		
1	41.3	18.54	81.46	7.0
2	12.6	5.66	75.80	3.3
3	11.9	5.34	70.46	2.0
4	15.7	7.05	63.41	1.1
filter	141.3	63.41		
	222.8			
		Site #8		
1	7.7	4.48	95.52	7.0
2	7.8	4.54	90.98	3.3
3	12.4	7.23	83.75	2.0
4	16.1	9.38	74.37	1.1
filter	127.6	74.36		
	171.6			

Figure 7.   Particle Size as a Function of Cumulative Percent
            Less Than a Stated Aerodynamic Diameter for
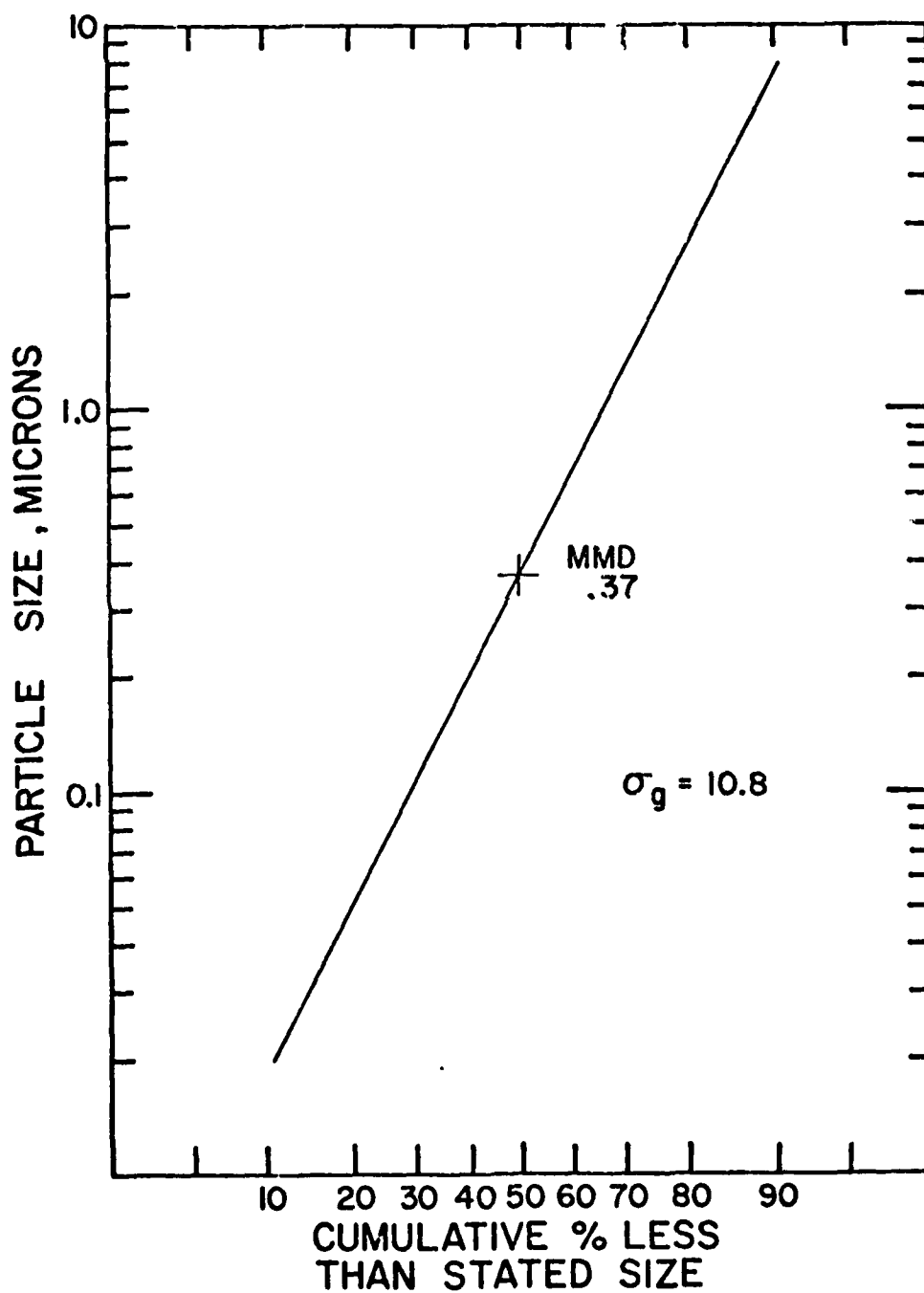   Site No. 2

Figure 8. Particle Size as a Function of Cumulative Percent Less Than a Stated Aerodynamic Diameter for Site No. 29
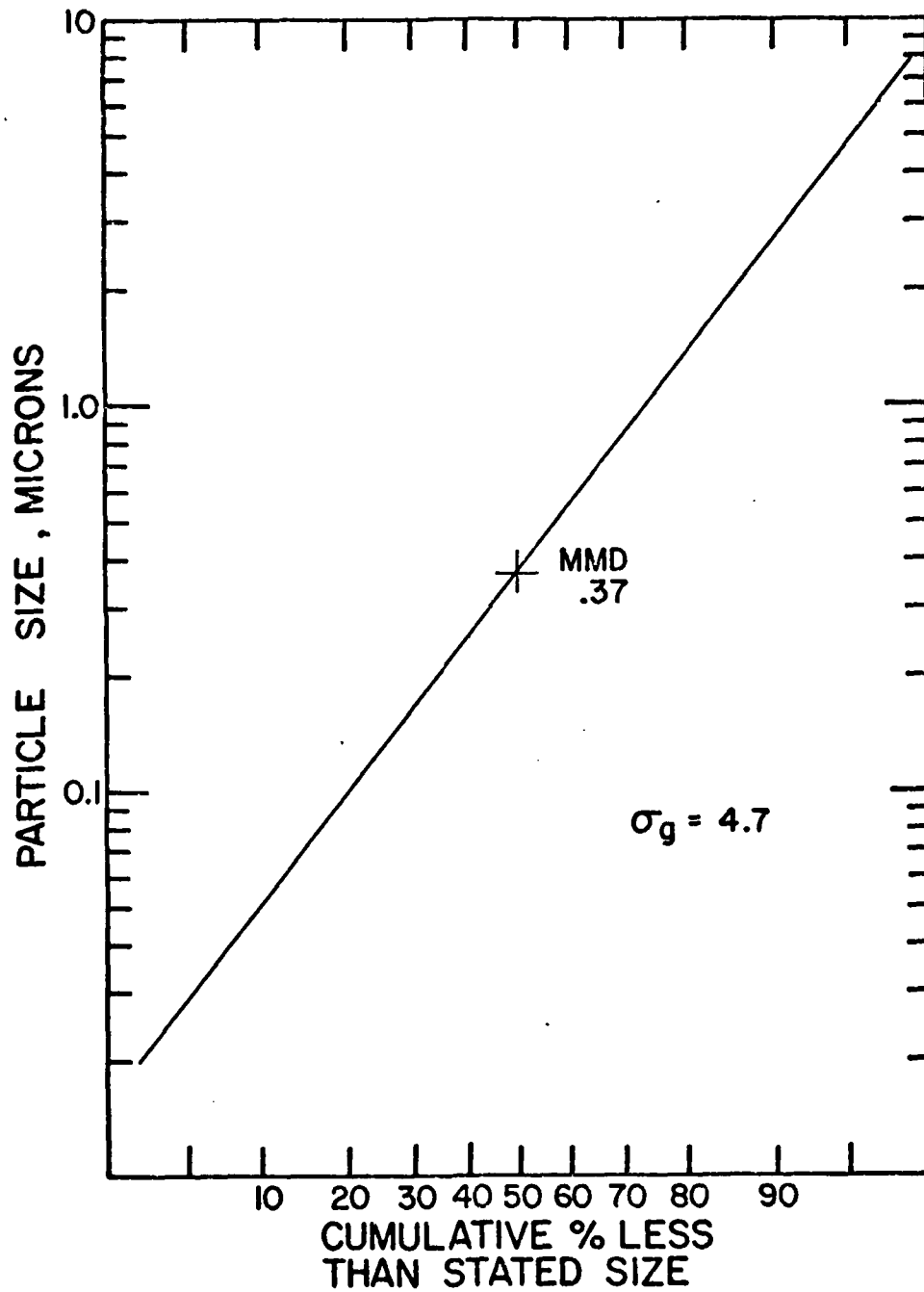
Figure 9. Particle Size as a Function of Cumulative Percent
Less Than a Stated Aerodynamic Diameter for
Site No. 613
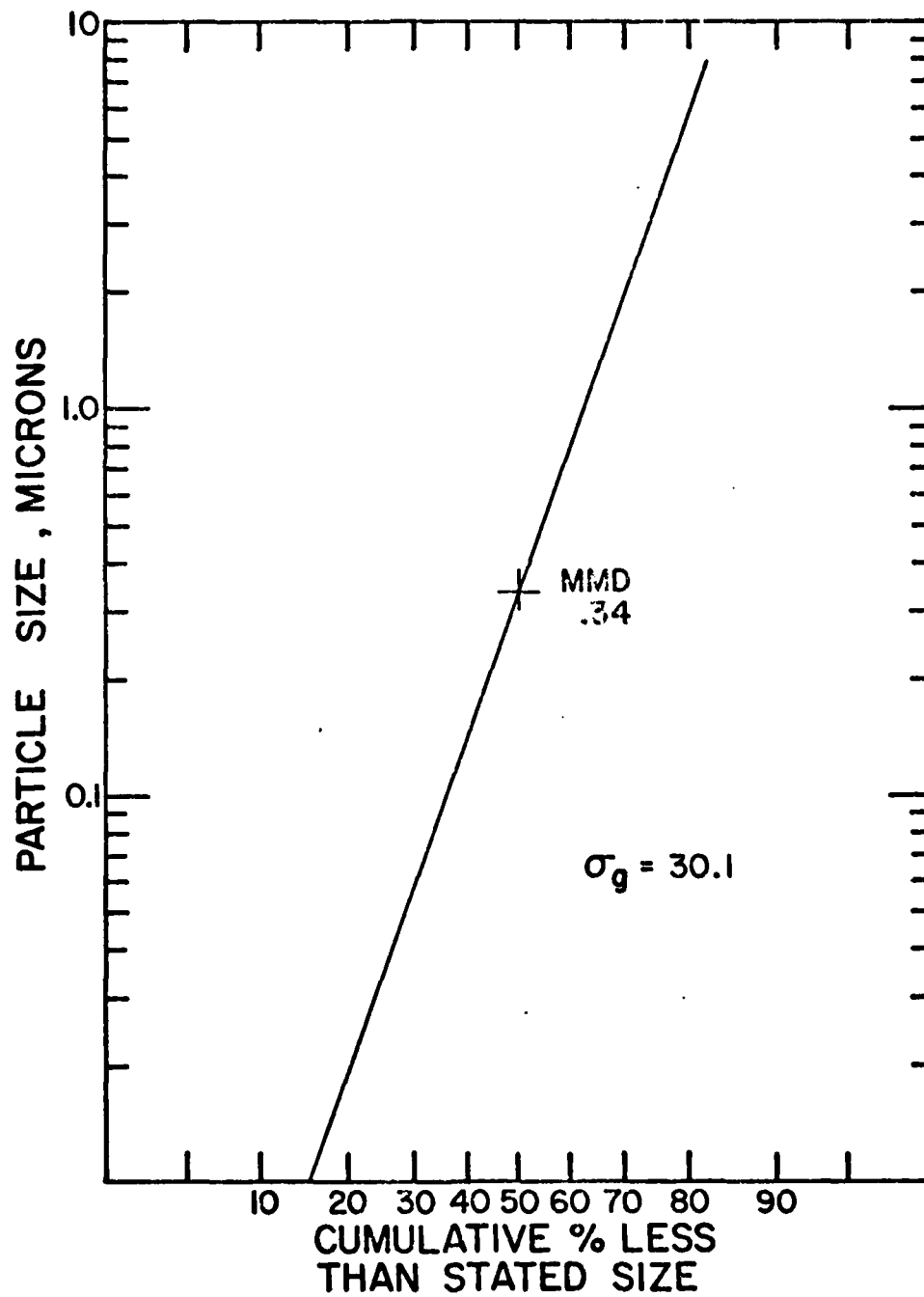
Figure 10. Particle Size as a Function of Cumulative Percent
Less Than a Stated Aerodynamic Diameter for
Site No. 8
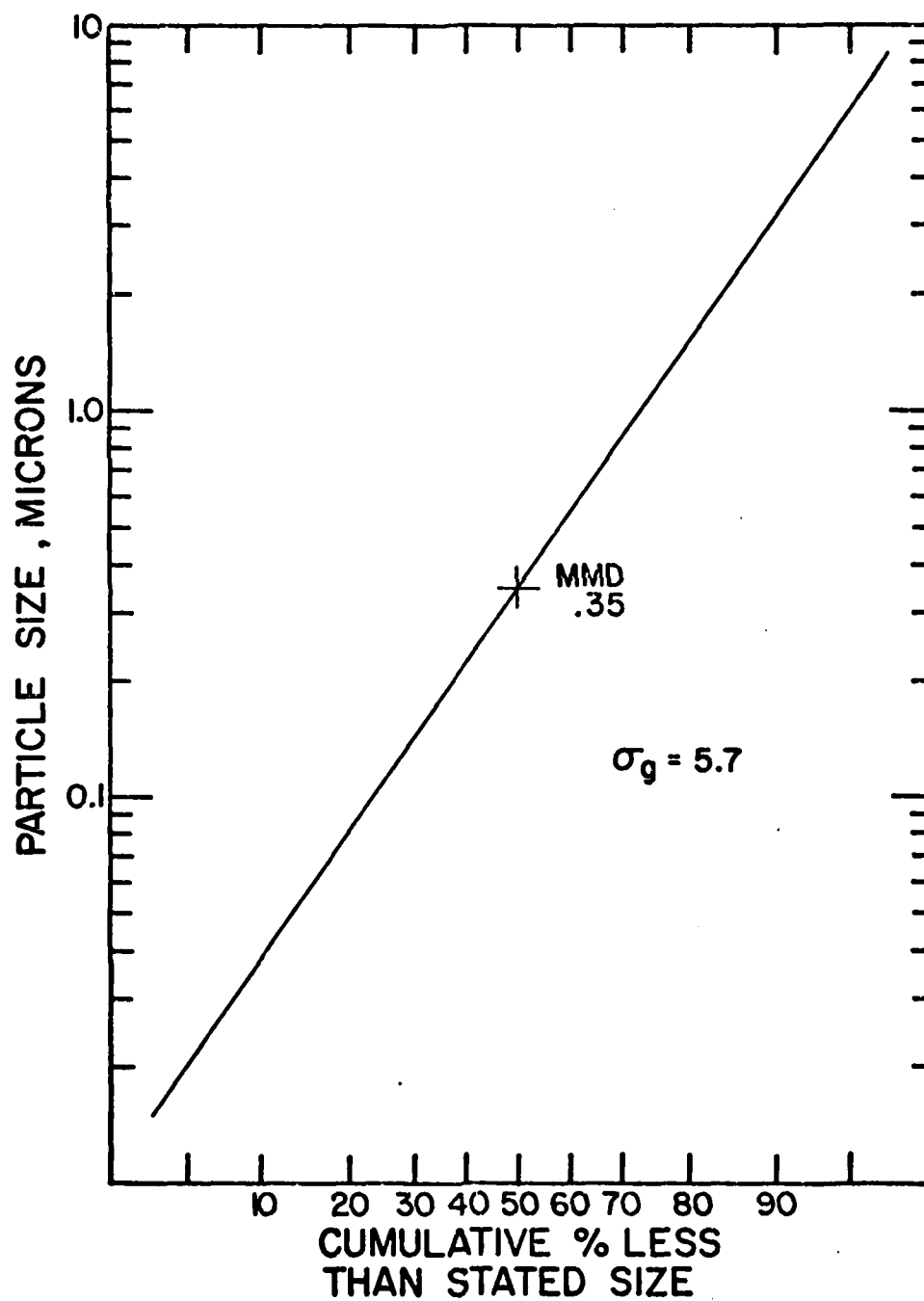
If Equations (1) and (2) are not equal, as is the case with a bimodal distribution, then Equation (3) is used to determine the standard deviation

$$\sigma_g = \left[\frac{84.13\% \text{ diameter}}{15.87\% \text{ diameter}}\right]^{1/2} \qquad (3)$$

OPTICAL MICROSCOPY

Equipment. The microscope used in this study was a Nikon S-kt with Koehler type illumination provided by a tungsten light source built into the microscope base. An apochromat 5 lens substage condensor, n.a. 1.25 was used. The Huygens' oculars were high mount type with 10X magnification. The following objectives were used: achromat, M5X, n.a. 0.1; achromat M10X, n.a. 0.25; achromat M20X, n.a. 0.4; and plan fluorite 40X, n.a. 0.75. Reflected light was provided by an epi-illuminator which added a 1.5X magnification factor. The microflex model AFM, automatic shutter system was fitted with either a 35 mm camera back or a type 545 Polaroid film holder. A Vivitar 49 mm polarizing lens was used over the substage illuminator. The total magnification obtained on the slides and prints is given in Table 9. Color slides were taken with Kodak Ektacolor 135, tungsten source film; black and white prints were made from Polaroid type 55, positive/negative film.

Table 9

FINAL MAGNIFICATIONS OF PARTICULATE ON 35 mm FILM AND
POLAROID PRINTS USING DIFFERENT MICROSCOPE OBJECTIVES

Objective	Microscope 10X occular 1.5X epi-illuminator	35 mm camera 1/2X relay lens 10X occular 1.5X epi-illuminator	Polaroid camera 1.3X relay lens 10X occular 1.5X epi-illuminator
5X	75	37	97.5
10X	150	75	195
20X	300	150	395
40X	600	300	780

Sample Preparation. A section containing five to ten
points of impaction was cut from each aluminum foil impaction
disk. While viewing the foil through a stereoscope, an
x-acto knife was used to carefully remove the particulate
and transfer it to a precleaned microscope slide. The
sample was covered with a #1-1/2 cover slip and placed on
a warm hot plate. A glass rod was used to run a bead of
melted Aroclor #5662 (W.J. McCrone Associates, Chicago,
Ill.) along the edge of the coverslip. Capillary action
carried the mounting medium under the coverslip. The slide
was removed from the hot plate, allowed to cool, then
microscopically examined. Microscope slides were prepared
of the particulate taken from each stage of the cascade
impactor, from industrial grab samples, and from soil
samples. The thermoplastic Aroclor #5662 is used in mounting
suspended particulate because its refractive index (1.660)
is higher than that of most environmental particles (1.50-1.55).

Biological type mounting media are unsuitable due to the
similarity of refractive indices with the majority of
airborne particulate matter.

Results. Thirty-two black and white photomicrographic
prints are presented herein to show the variety of inorganic
and biological materials found in the air. Table 10
identifies each of these pictures.

ATOMIC ABSORPTION ANALYSIS

Equipment. The atomic absorption measurements were
obtained with a Varian Techtron AAS-1200 (Springvale, Vic.,
Australia). Operating parameters for the hollow cathode
lamps are given by Table 11. Table 12 lists the absorption
wavelengths and detection limits for each element analyzed.

Sample Preparation. All samples were ashed in an LFE
(LFE Corporation, 1601 Tzapelo Rd., Waltham, Mass 02154)
Model 505 low temperature asher (LTA) operating at 255 watts
RF. One half of each backup filter (2 per site) was cut
into narrow strips (approximately 2 x 6 cm) and placed into
aluminum foil boats. The samples, along with a clean
cellulose filter paper, to be used as a blank, were ashed
for 16 hours. The resulting ash was dissolved in 2.5 ml of
10N HNO_3 and diluted to 25 ml in a volumetric flash. Each
aluminum foil disk was cut into eight pieces and each seg-
ment was ashed for 30 minutes. The foil was then placed
in 10N HNO_3 and the particulate scraped off with a poly-
ethylene scraper. The scraper and foil were rinsed with

Table 10

LIST OF PHOTOMICROGRAPHS OF AIRBORNE PARTICULATE, INDUSTRIAL GRAB SAMPLES, AND SOILS

Photo	Sample	Magnification
	Airborne Particulate Collected with Cascade Impactor in Dayton, Ohio	
1.	Site 2, 1st stage	195x
2.	Site 2, 1st stage	390x
3.	Site 29, 1st stage	195x
4.	Site 29, 1st stage	390x
5.	Site 613, 1st stage	195x
6.	Site 613, 1st stage	390x
7.	Site 613, 1st stage	390x
8.	Site 8, 1st stage	390x
9.	Site 8, 1st stage	390x
10.	Site 8, 2nd stage	390x
11.	Site 8, 2nd stage	390x
	Industrial Grab Samples and Soils from Dayton, Ohio	
12.	Northwood Asphalt, bottom of hopper	185x
13.	Armco, Piqua	195x
14.	American Aggregate	195x
15.	Dura-crete - road sample	195x
16.	Early and Daniel, dump beans	195x
17.	Early and Daniel, dump corn	195x

Table 10 (continued)

LIST OF PHOTOMICROGRAPHS OF AIRBORNE PARTICULATE
INDUSTRIAL GRAB SAMPLES AND SOILS

Photo	Sample	Magnification
18.	NIBCO baghouse on shotblast from dump hopper	390x
19.	NIBCO sand handling system before scrubing	195x
20.	DP&L, Unit 4, hopper 16 fly ash	195x
21.	DP&L, Coal before being pulverized	390x
22.	DP&L, bottom ash discharge outlet	195x
23.	SWPC, clinker coaler	195x
24.	SWPC, fallout from kiln	195x
25.	SWPC, alkaline bypass material	195x
26.	South Montgomery County Municipal Incinerator, ash	97.5x
27.	Street sweepings, Needmore, Linden, Harshman Taylorsville Roads	195x
28.	Street sweepings, McArthur, Harshman, Yolandia, Nicholas Roads	195x
29.	Crosby silt loam, Butler Township	195x
30.	Crosby silt loam, Darke County	195x
31.	Ragsdale silt clay, Greene County	195x
32.	Miami silt loam, Montgomery County	195x

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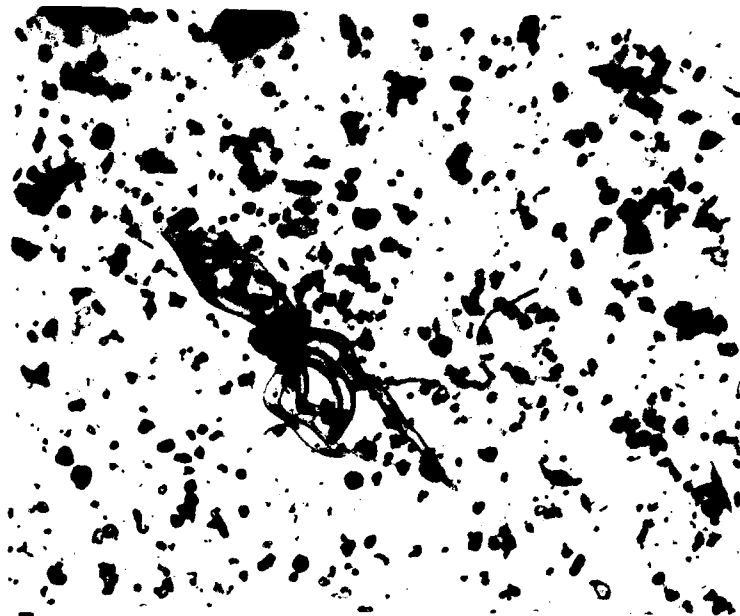
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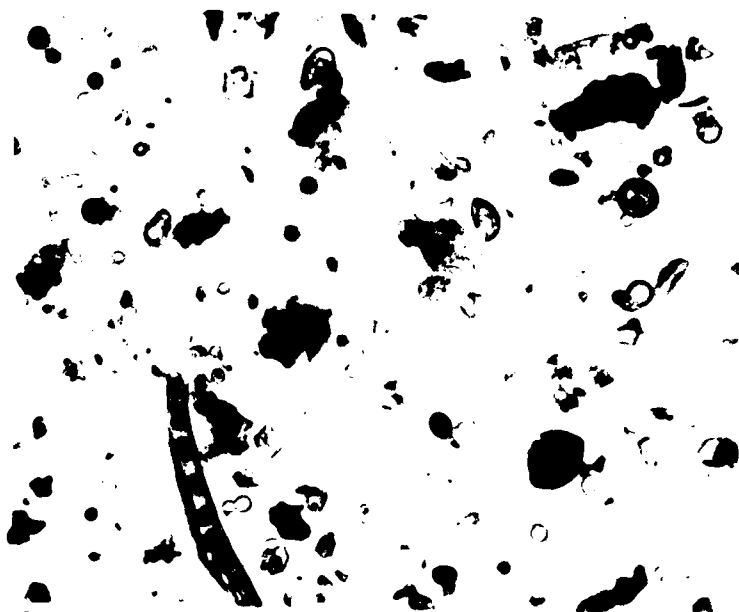
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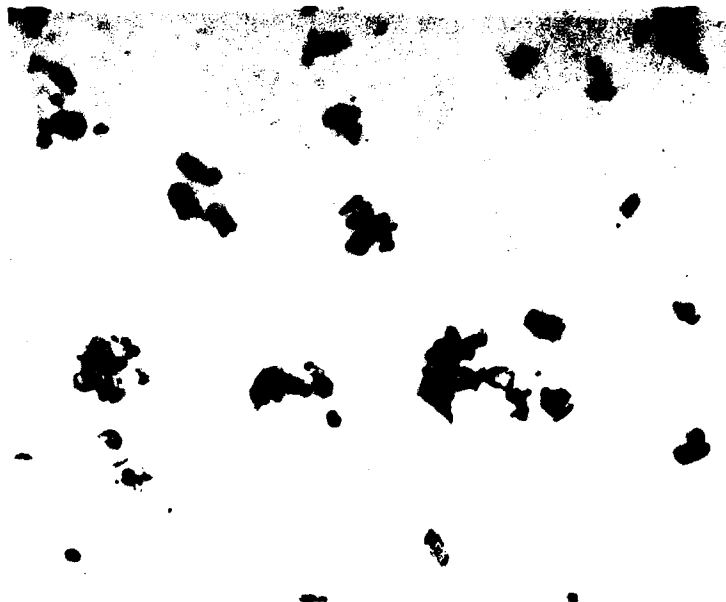
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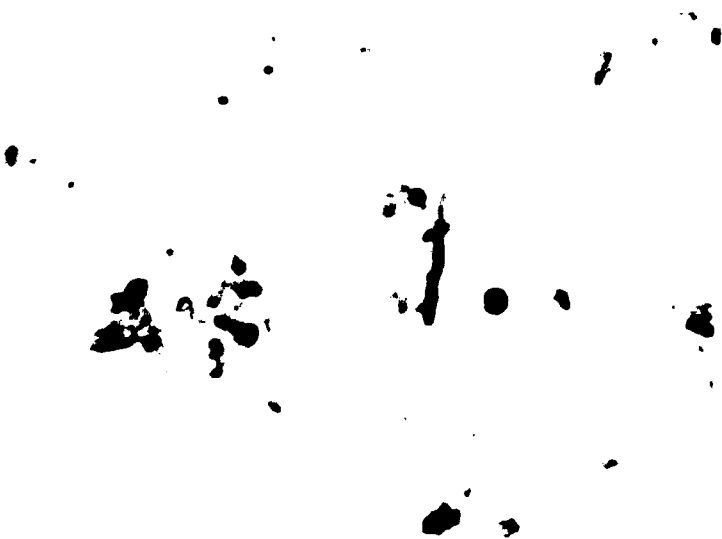
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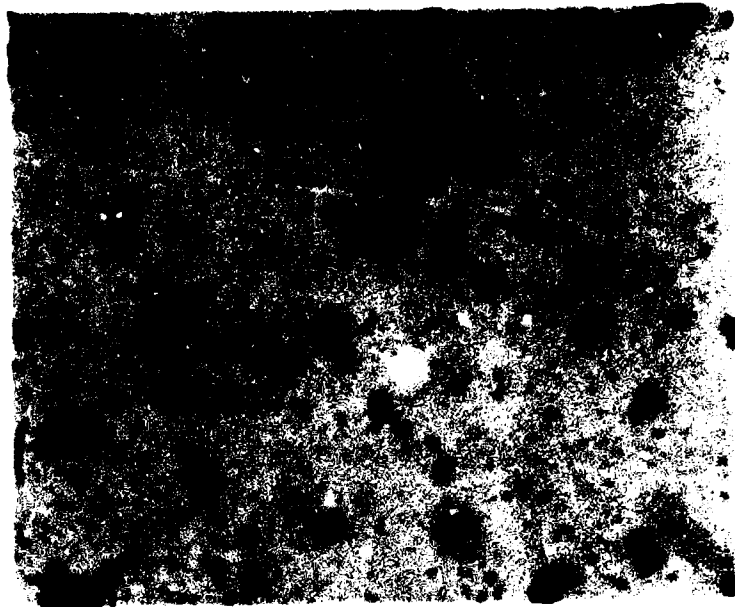
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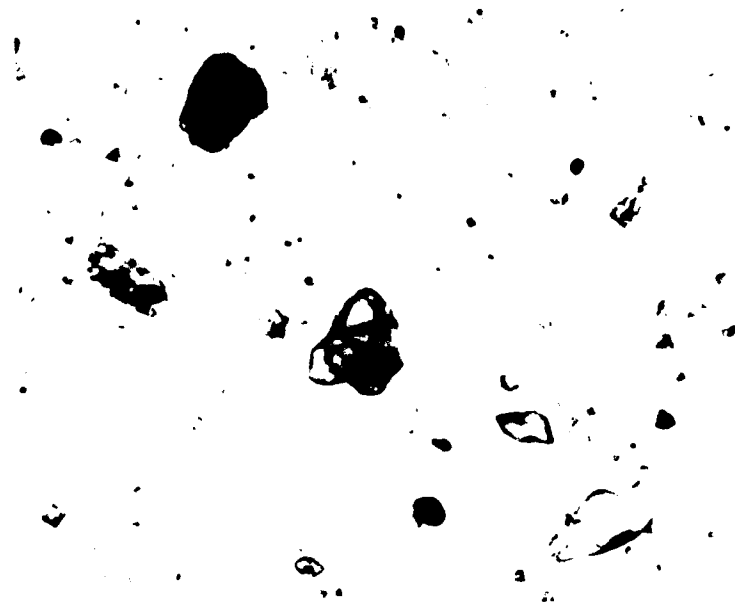
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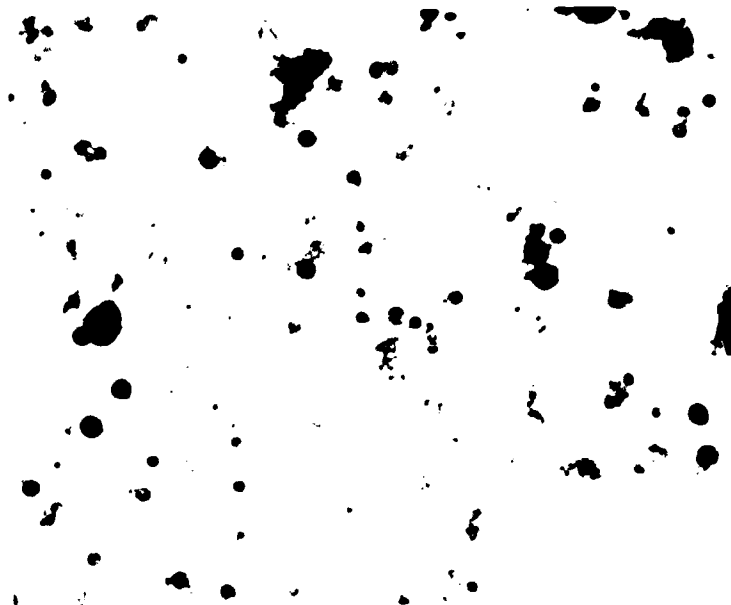
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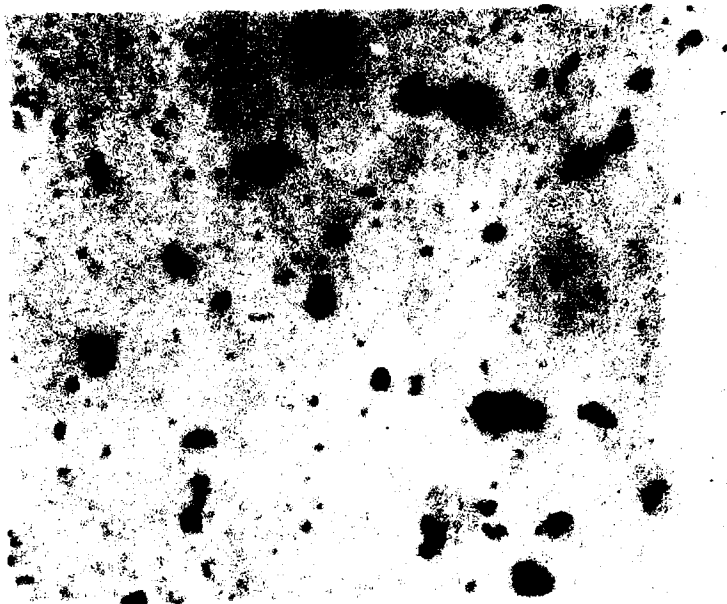
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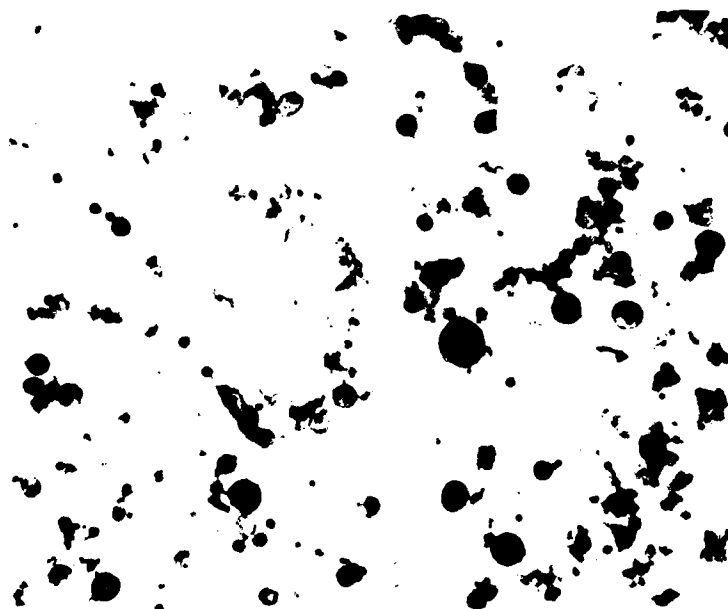
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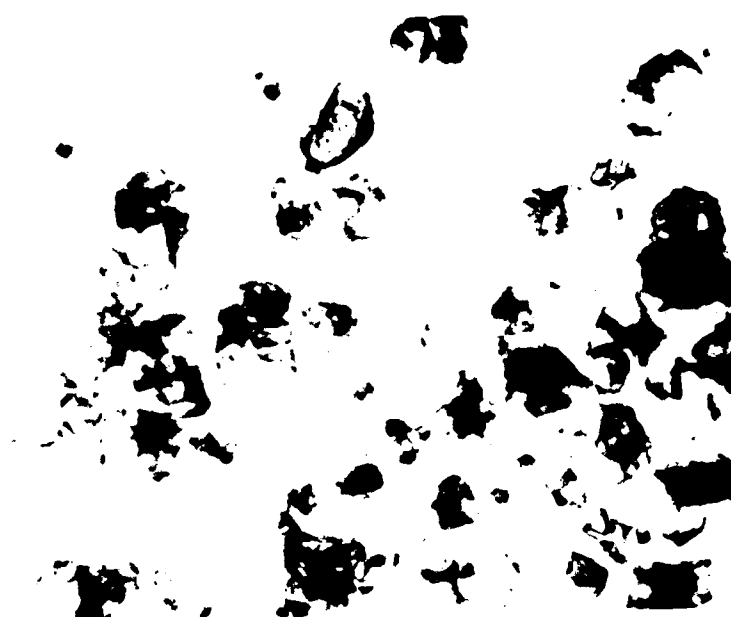
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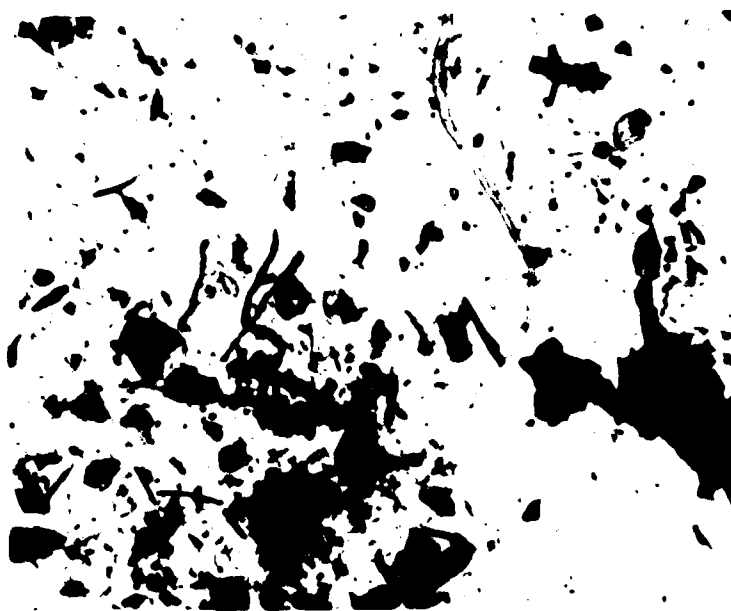
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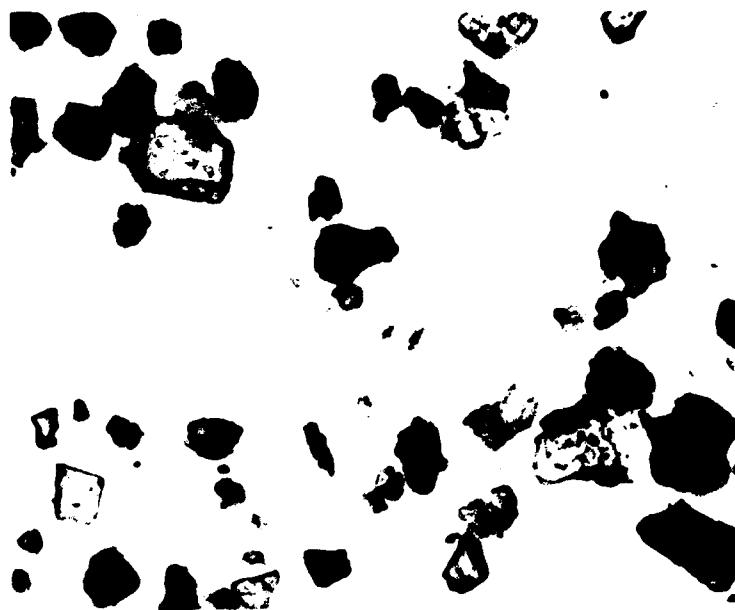
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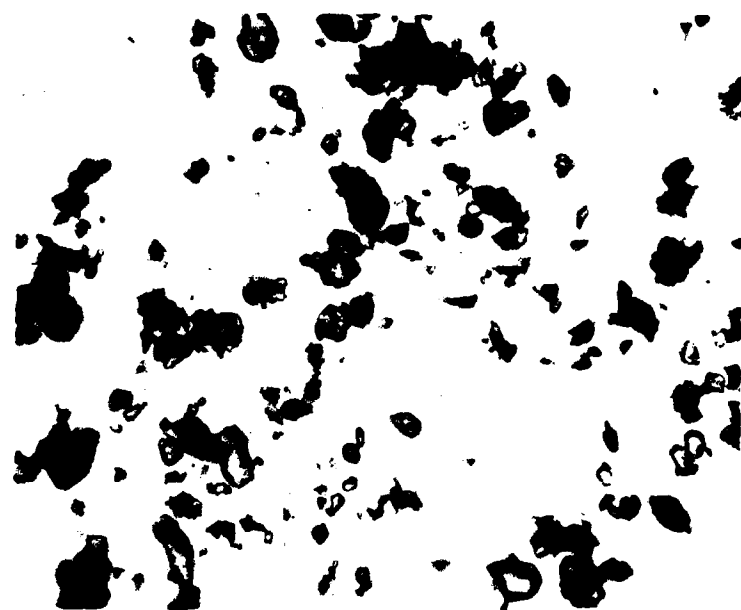
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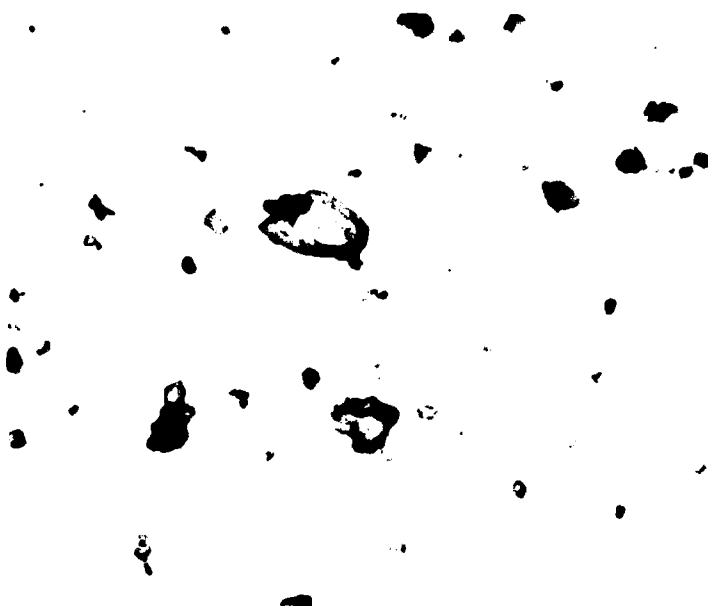
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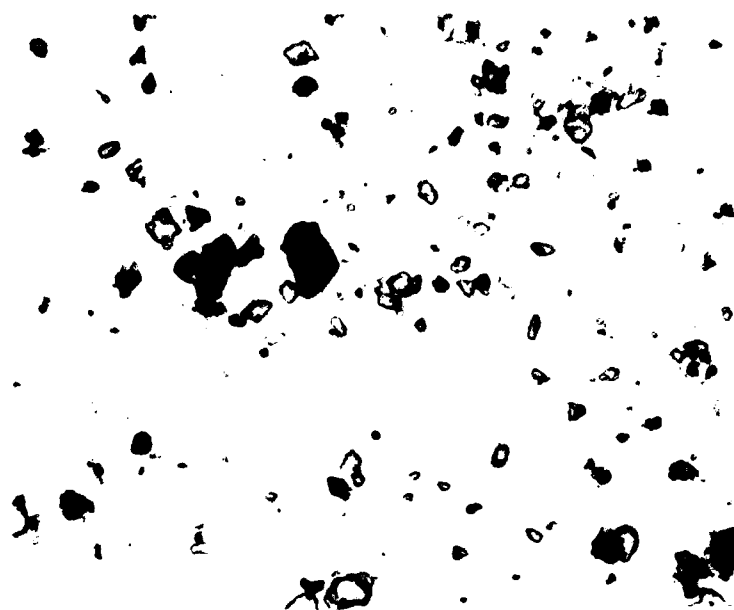
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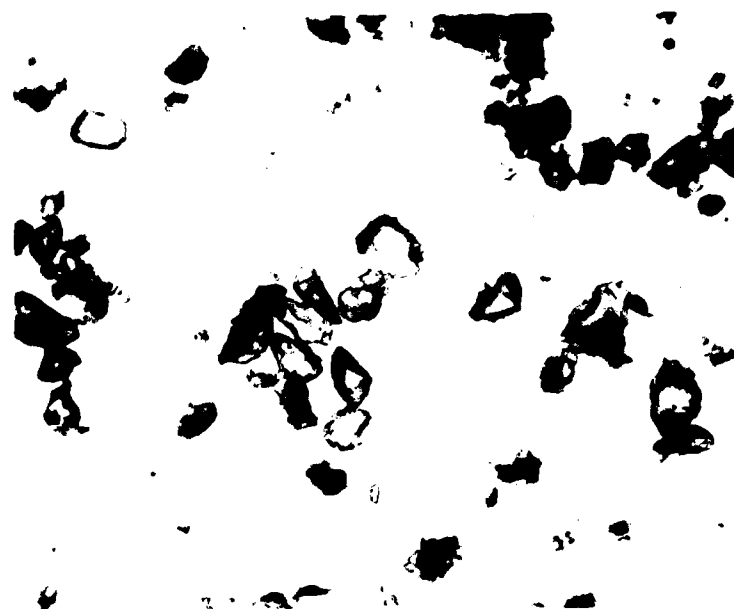
32

Table 11

OPERATING PARAMETERS OF HOLLOW CATHODE LAMPS
USED IN ATOMIC ABSORPTION SPECTROSCOPY

Element	Cr	Fe	Mn	Ni	Pb	Zn
lamp current	5 ma	5 ma	5 ma	5 ma	6 ma	5 ma
fuel	C_2H_2	C_2H_2	C_2H_2	C_2H_2	C_2H_2	C_2H_2
support	air	air	air	air	air	air
flame stoichiometry	reducing	oxidizing	oxidizing	oxidizing	oxidizing	oxidizing

Table 12

ABSORPTION WAVELENGTH AND DETECTION LIMITS
FOR ATOMIC ABSORPTION SPECTROSCOPY

Element	Wavelength (nm)	Spectral Band Pass (mm)	Working Range (μg/ml)	Sensitivity (μg/ml)	Detection Limit (μg/ml)
Cr	357.9	0.2	2.0-8.0	0.055	0.005
Fe	248.3	0.2	2.5-10	0.062	0.005
Mn	279.5	0.2	1.0-4.0	0.024	0.003
Ni	232.0	0.2	3-12	0.066	0.008
Pb	217.0	1.0	5-10	0.11	0.02
Zn	213.9	0.2	0.4-1.6	0.009	0.002

distilled water and the total solution (approximately

50 ml) was slowly evaporated on a hot plate to 15 ml,

then diluted in a 25 ml volumetric flask with distilled

water.

To measure sample recovery, 0.1000 g of the U.S.

Geological Survey (Washington, D.C.) standard rock W-1 was

prepared for analysis in the same manner as the particulate

samples. The standard was placed in an aluminum boat and

dry ashed for 30 minutes. The residue was diluted with

10N HNO_3 and distilled water and the liquid was then reduced

in volume to 15 ml by placing the sample vessel on a hot

plate. The resultant solution was rediluted to 25 ml in a

volumetric flash and aliquots of this were analyzed using

Atomic Absorption Spectroscopy. Recoveries of the metals in

the W-1 sample which were achieved using these methods are

given in Table 13. These recoveries were used to correct the

results of the particulate analyses.

Results. The results of the atomic absorption measure-

ments, corrected for elemental recovery based on analyses

of the W-1 standard, are given in Tables 14 through 19.

This data is also presented graphically in Figures 11 through

15 which present the percent distribution of each metal over

the four impaction disks and backup filters. The fraction

of metal as a function of total particulate on any single

collection stage is presented in Figures 16 through 20.

Table 13

RECOVERIES FOR ANALYSIS OF W-1 BY
ATOMIC ABSORPTION SPECTROSCOPY

	ppmw	µg/g analyzed	µg/ml	µg/ml found	% recovery
Cr	120	12.0	0.45	0.30	66.7
Fe	7.77%	7770	311.0	224	72.0
Mn	1320	132	5.28	4.0	76.0
Ni	78	7.8	0.31	0.022	71.0
Pb	8	0.8	0.03	0.020	66.0
Zn	82	8.2	0.33	0.27	63.6

Table 14

RESULTS OF CHROMIUM ANALYSIS BY
ATOMIC ABSORPTION SPECTROSCOPY

Site		Total Partic. $\mu g/m^3$	$\mu g/m^3$ Cr	Cr Distrib. %	% Cr in Total Partic/Stage
2	F	187.8	0.005	14.3	0.0027
	4	13.7	0.008	22.9	0.058
	3	19.6	0.006	17.1	0.035
	2	23.2	0.008	22.9	0.034
	1	27.6	0.008	22.9	0.029
Total		271.6	0.035		
			129 µg/g		0.013 % Cr in total sample
29	F	170.2	0.016	34.0	0.0094
	4	23.8	0.017	14.9	0.029
	3	13.0	0.008	17.0	0.062
	2	11.5	0.008	17.1	0.070
	1	6.8	0.008	17.0	0.120
Total		225.3	0.047		
			209 µg/g		0.021 % Cr in total sample
613	F	173.4	ND	--	--
	4	19.3	0.0025	21.4	0.014
	3	14.6	0.0063	53.8	0.043
	2	15.5	0.0016	13.7	0.010
	1	50.7	0.0013	11.1	0.002
Total		273.4	0.0117		
			43 µg/g		0.004 % Cr in total sample
8	F	156.4	ND	--	--
	4	19.8	0.0028	15.3	0.014
	3	15.2	0.0006	3.28	0.004
	2	9.6	0.0067	36.6	0.07
	1	9.4	0.0082	44.8	0.087
Total		210.6	0.0183		
			87 µg/g		0.0087 % Cr in total sample

Table 15

RESULTS OF IRON ANALYSIS BY
ATOMIC ABSORPTION SPECTROSCOPY

Site		Total Partic. $\mu g/m^3$	$\mu g/m^3$ Fe	Fe Distrib. %	% Fe in Total Partic/Stage
2	F	187.8	0.286	56.5	0.15
	4	13.7	0.025	4.9	0.18
	3	19.6	0.028	5.3	0.14
	2	23.2	0.059	11.7	0.25
	1	27.6	0.108	21.3	0.39
Total		271.9	0.506		
			1865 $\mu g/g$		0.18% Fe in sample
29	F	170.2	0.157	49.7	0.09
	4	23.8	0.033	10.4	0.14
	3	13.0	0.016	5.1	0.12
	2	11.5	0.036	8.2	0.31
	1	6.8	0.074	12.1	1.08
Total		225.3	0.316		
			1400 $\mu g/g$		0.140 % Fe in sample
613	F	173.4	0.238	60.9	0.14
	4	19.3	0.028	7.2	0.14
	3	14.6	0.019	4.9	0.13
	2	15.5	0.028	7.2	0.18
	1	50.7	0.078	19.9	0.15
Total		273.4	0.391		
			1430 $\mu g/g$		0.14 % Fe in sample
8	F	136.6	0.666	83.8	0.42
	4	19.8	0.031	3.9	0.16
	3	15.2	0.009	1.1	0.06
	2	9.6	0.028	3.5	0.29
	1	9.4	0.061	7.7	0.65
Total		210.6	0.795		
			3780 $\mu g/g$		0.37 % Fe in sample

Table 16

RESULTS OF MANGANESE ANALYSIS BY
ATOMIC ABSORPTION SPECTROSCOPY

Site		Total Partic. $\mu g/m^3$	$\mu g/m^3$ Mn	Mn Distrib. %	% Mn in Total Partic/Stage
2	F	187.8	0.012	55.8	0.0064
	4	13.7	0.0015	7.0	0.071
	3	19.6	0.001	4.6	0.0031
	2	23.2	0.003	14.0	0.013
	1	27.6	0.004	18.6	0.014
Total		271.9	0.0215		
			79 µg/g		0.008 % Mn in total sample
29	F	170.2	0.064	88.2	0.038
	4	23.8	0.0006	0.83	0.0025
	3	13.0	0.001	1.4	0.0077
	2	11.5	0.003	4.1	0.026
	1	6.8	0.004	5.5	0.059
Total		225.3	0.0726		
			322 µg/g		0.032 % Mn in total sample
613	F	173.4	0.075	85.2	0.043
	4	19.3	0.002	2.3	0.01
	3	14.6	0.001	1.1	0.007
	2	15.5	0.002	2.3	0.013
	1	50.7	0.008	9.1	0.016
Total		273.4	0.088		
			321 µg/g		0.032 % Mn in total sample
8	F	156.6	0.041	82.0	0.026
	4	19.8	0.001	2.0	0.001
	3	15.2	0.0003	0.6	0.002
	2	9.6	0.003	10.0	0.052
	1	9.4	0.002	4.0	0.002
Total		210.6	0.050		
			237 µg/g		0.024 % Mn in total sample

Table 17

RESULTS OF NICKEL ANALYSIS BY
ATOMIC ABSORPTION SPECTROSCOPY

Site	$\mu g/m^3$ Ni
2	0.00258
29	0.0200
613	0.00258
8	0.0080

Nickel was only detected on the backup filters.

Table 18

RESULTS OF LEAD ANALYSIS BY
ATOMIC ABSORPTION SPECTROSCOPY

Site		Total Partic. $\mu g/m^3$	$\mu g/m^3$ Pb	Pb Distrib. %	% Pb in Total Partic/Stage
2	F	187.8	0.55	76.5	0.29
	4	13.7	0.038	5.3	0.28
	3	19.6	0.033	4.6	0.17
	2	23.2	0.055	7.7	0.24
	1	27.6	0.043	6.0	0.16
Total		271.9	0.719		
			2644 µg/g		0.26 % Pb in total sample
29	F	170.2	0.8	79.2	0.47
	4	23.8	0.05	4.9	0.21
	3	13.0	0.037	3.7	0.28
	2	11.5	0.06	5.9	0.52
	1	6.8	0.063	6.2	0.93
Total		225.3	1.01		
			4500 µg/g		0.45 % Pb in total sample
613	F	173.4	0.42	21.6	0.24
	4	19.3	0.05	8.5	0.26
	3	14.6	0.03	5.1	0.20
	2	15.5	0.043	7.3	0.28
	1	50.7	0.043	7.3	0.28
Total		273.4	0.586		
			2143 µg/g		0.21% Pb in total sample
8	F	156.6	0.61	78.8	0.39
	4	19.8	0.044	5.7	0.22
	3	15.2	0.054	7.0	0.36
	2	9.6	0.032	4.1	0.33
	1	9.4	0.034	4.4	0.36
Total		210.6	0.774		
			3675 µg/g		0.37% Pb in total sample

Table 19

RESULTS OF ZINC ANALYSIS BY
ATOMIC ABSORPTION SPECTROSCOPY

Site		Total Partic. $\mu g/m^3$	$\mu g/m^3$ Zn	Zn Distrib. %	% Zn in Total Partic/Stage
2	F	187.8	0.063	55.3	0.034
	4	13.7	0.015	13.2	0.109
	3	19.6	0.006	5.3	0.031
	2	23.2	0.012	10.5	0.052
	1	26.7	0.018	15.8	0.065
Total		271.9	0.114		
			419 µg/g		0.042 % Zn in total sample
29	F	170.2	0.091	49.7	0.053
	4	23.8	0.016	8.7	0.067
	3	13.0	0.01	5.5	0.077
	2	11.5	0.023	12.6	0.20
	1	6.8	0.043	23.5	0.63
Total		225.3	0.183		
			813 µg/g		0.081 % Zn in total sample
613	F	173.4	0.015	22.1	0.001
	4	19.3	0.016	23.5	0.083
	3	14.6	0.011	16.2	0.075
	2	15.5	0.01	14.7	0.064
	1	50.7	0.016	23.5	0.032
Total		273.4	0.068		
			249 µg/g		0.025 % Zn in total sample
8	F	156.6	0.055	49.6	0.035
	4	19.8	0.013	11.7	0.066
	3	15.2	0.008	7.2	0.053
	2	9.6	0.017	15.3	0.177
	1	9.4	0.018	16.2	0.192
Total		210.6	0.111		
			527 µg/g		0.053 % Zn in total sample

Figure 11. Percent of Total Chromium Distributed Over the Four Impaction Stages and Backup Filters
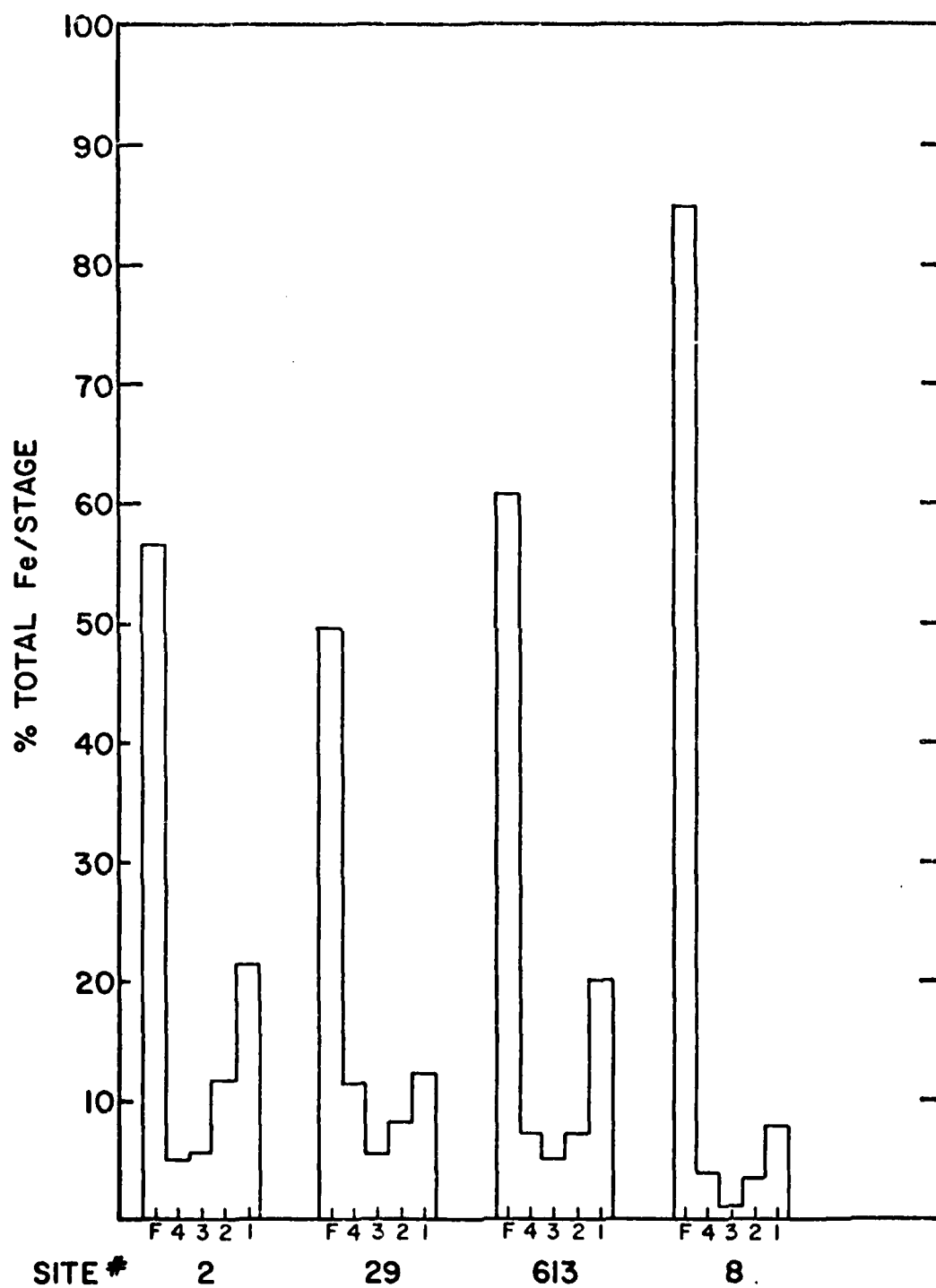
Figure 12.   Percent of Total Iron Distributed Over the Four
Impaction Stages and Backup Filters
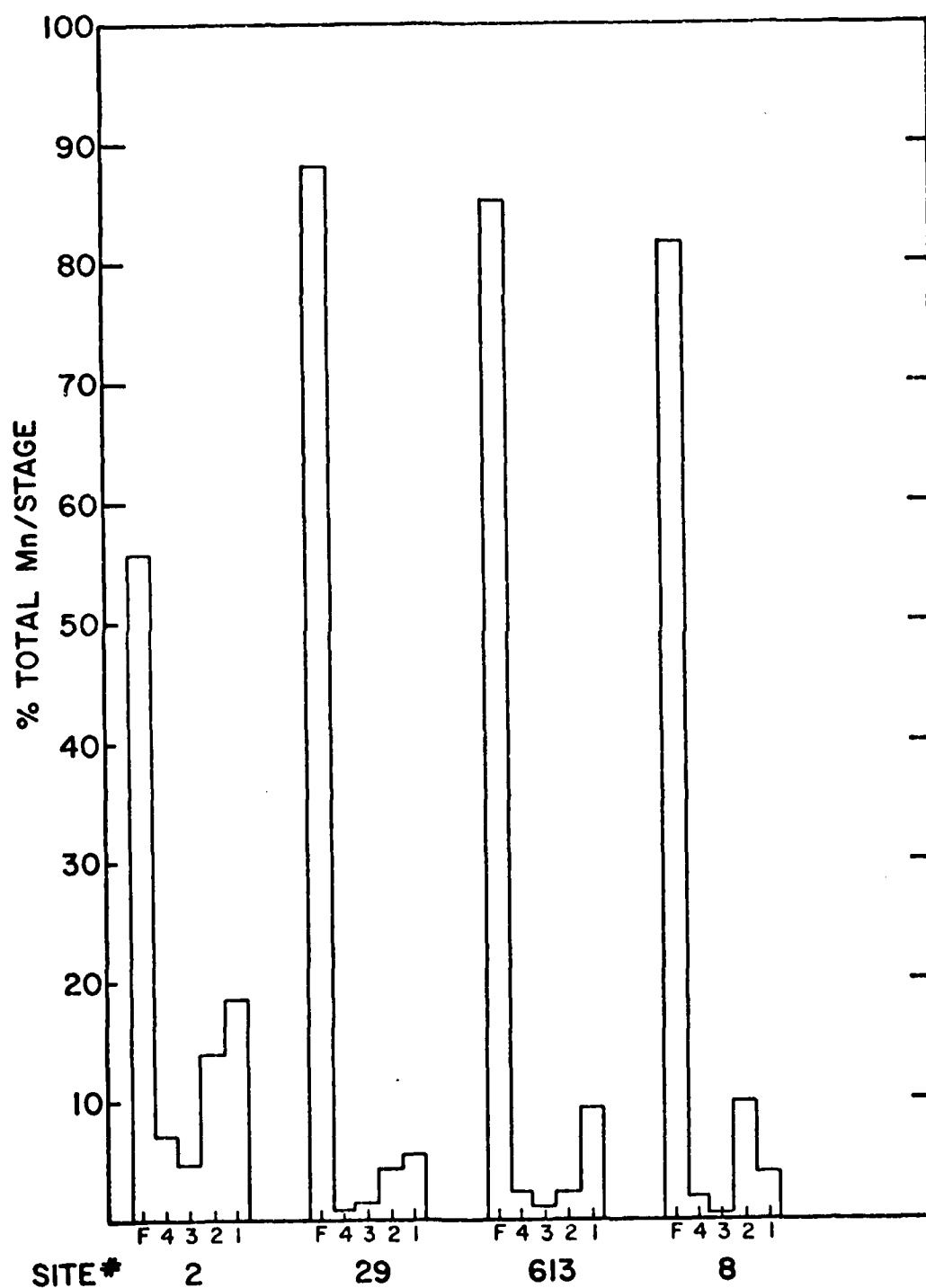
Figure 13. Percent of Total Manganese Distributed Over the
Four Impaction Stages and Backup Filters
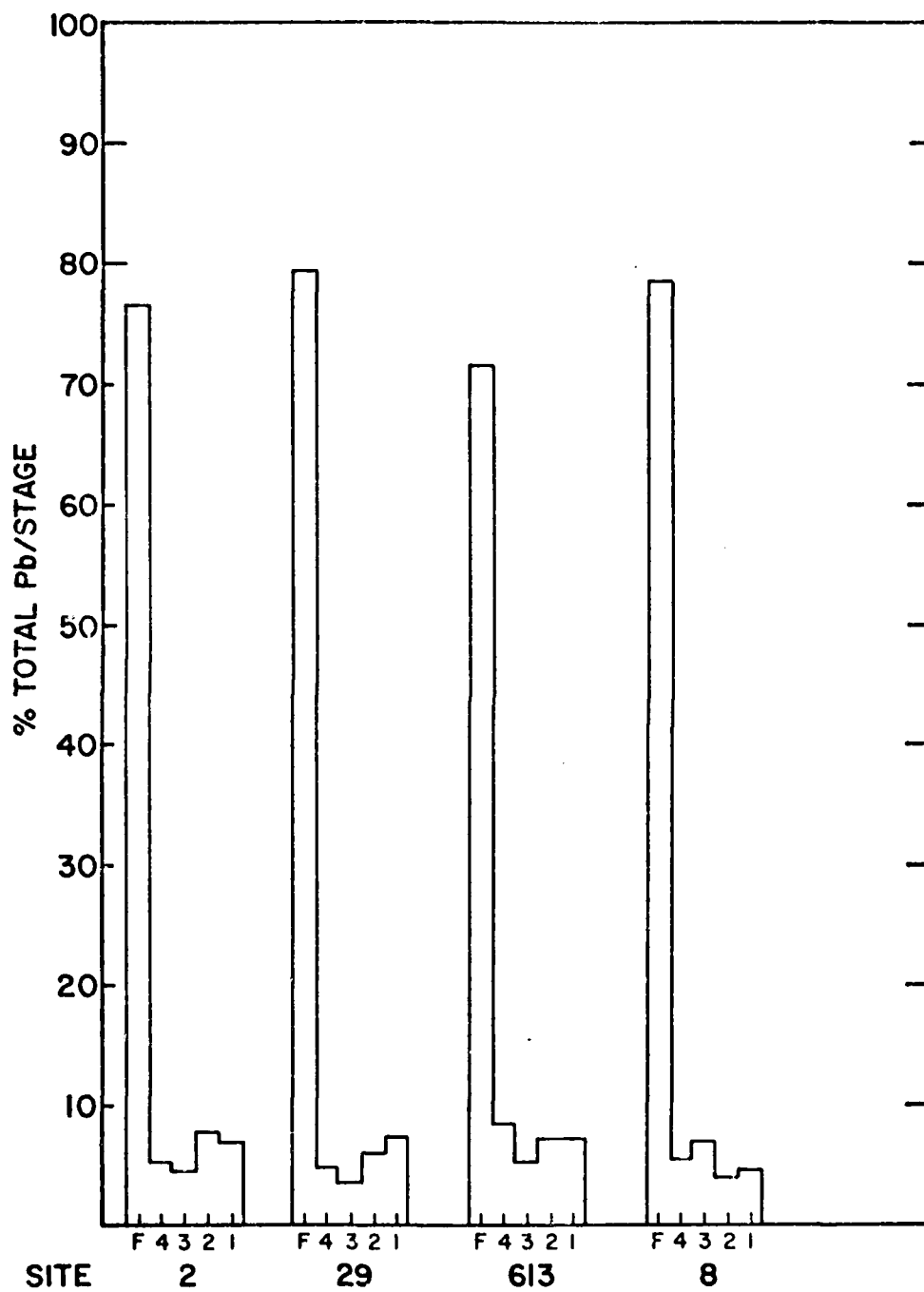
Figure 14.   Percent of Total Lead Distributed Over the Four
Impaction Stages and Backup Filters

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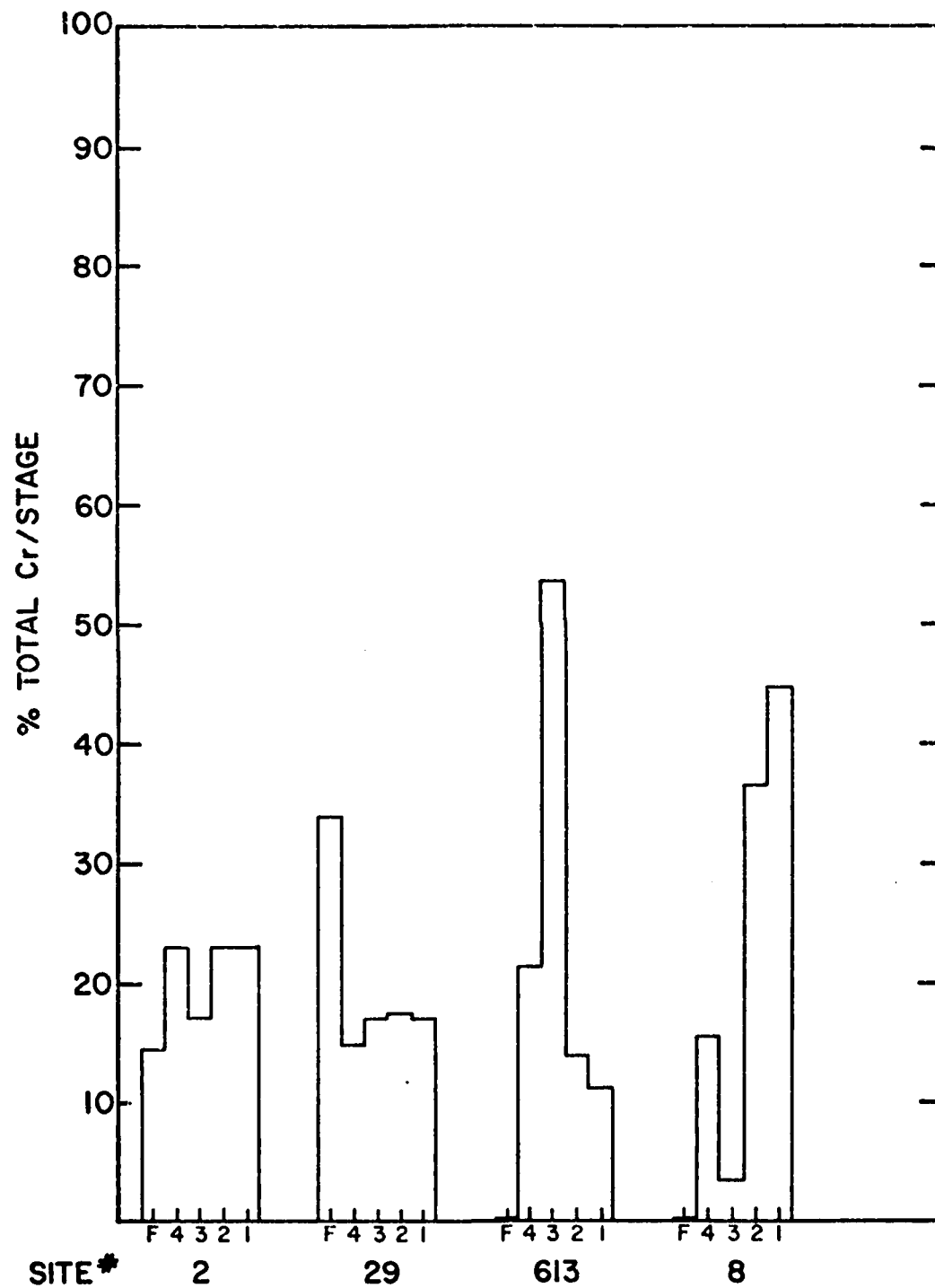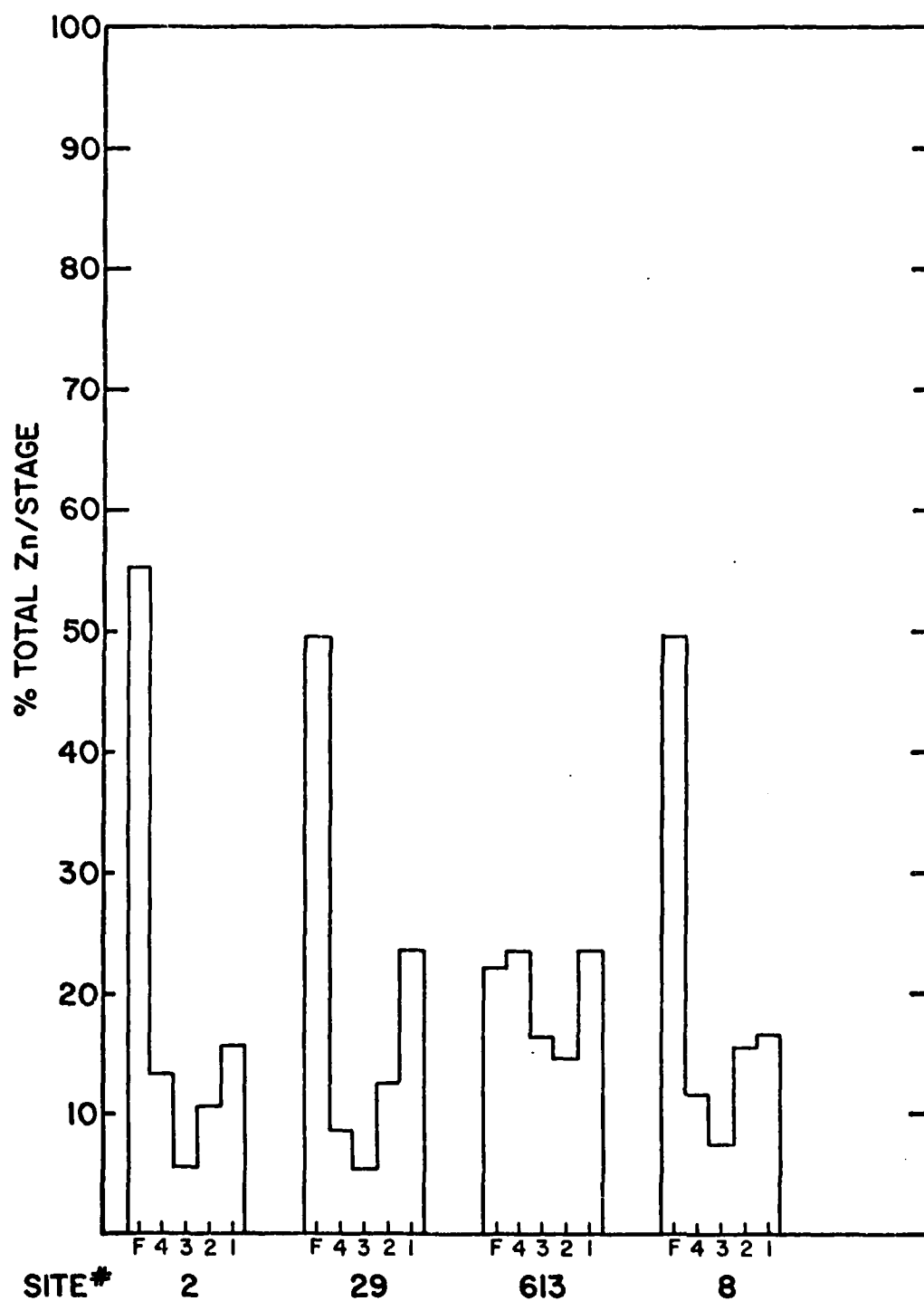
Figure 15.   Percent of Total Zinc Distributed Over the Four
Impaction Stages and Backup Filters

Figure 16.   Percent of Total Particulate   Collected on Each
            Impaction Stage and on Backup Filters as Cr

Figure 17. Percent of Total Particulate Collected on Each
Impaction Stage and on Backup Filters as Fe
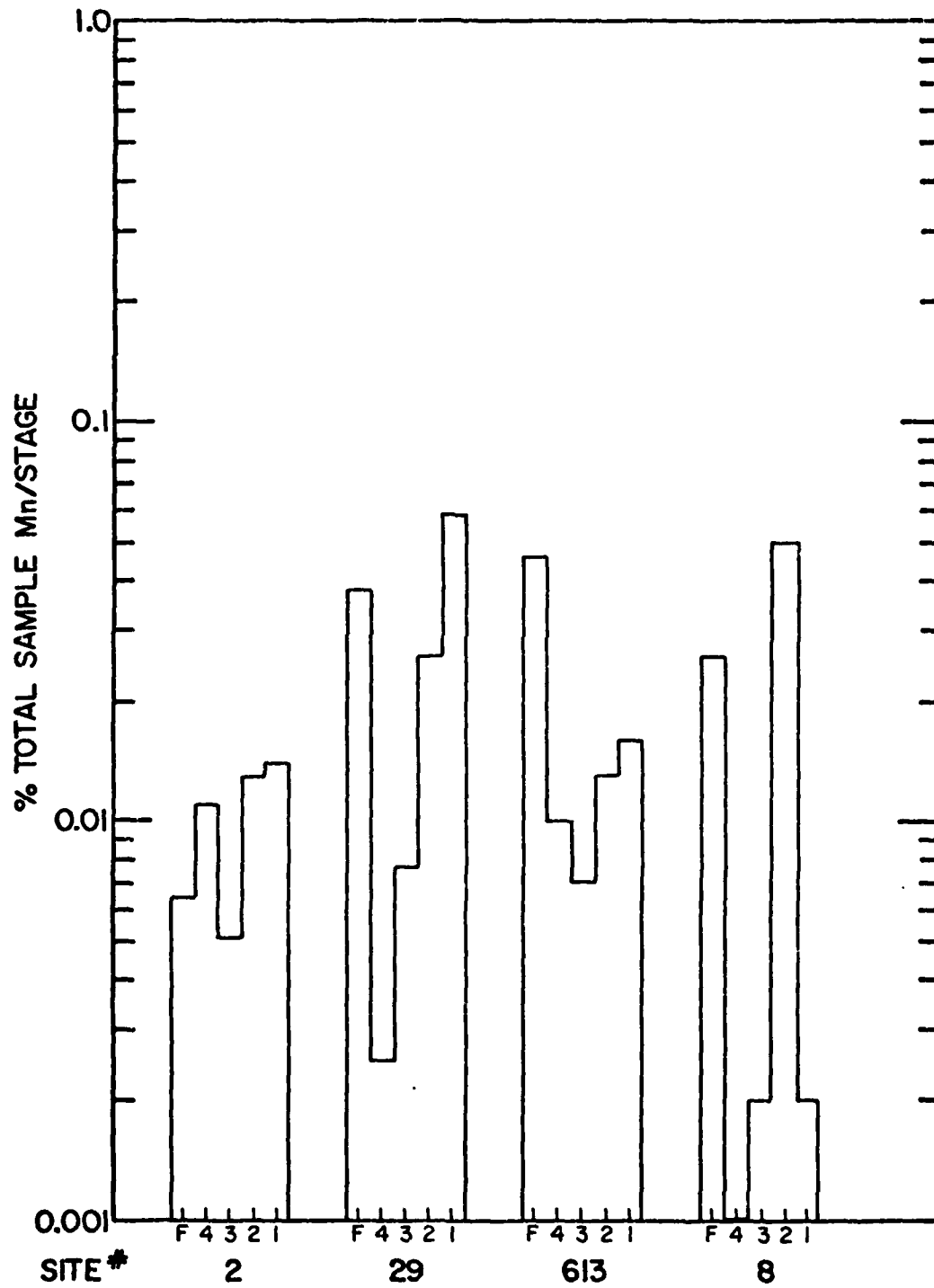
Figure 18.   Percent of Total Particulate Collected on Each
Impaction Stage and on Backup Filters as Mn
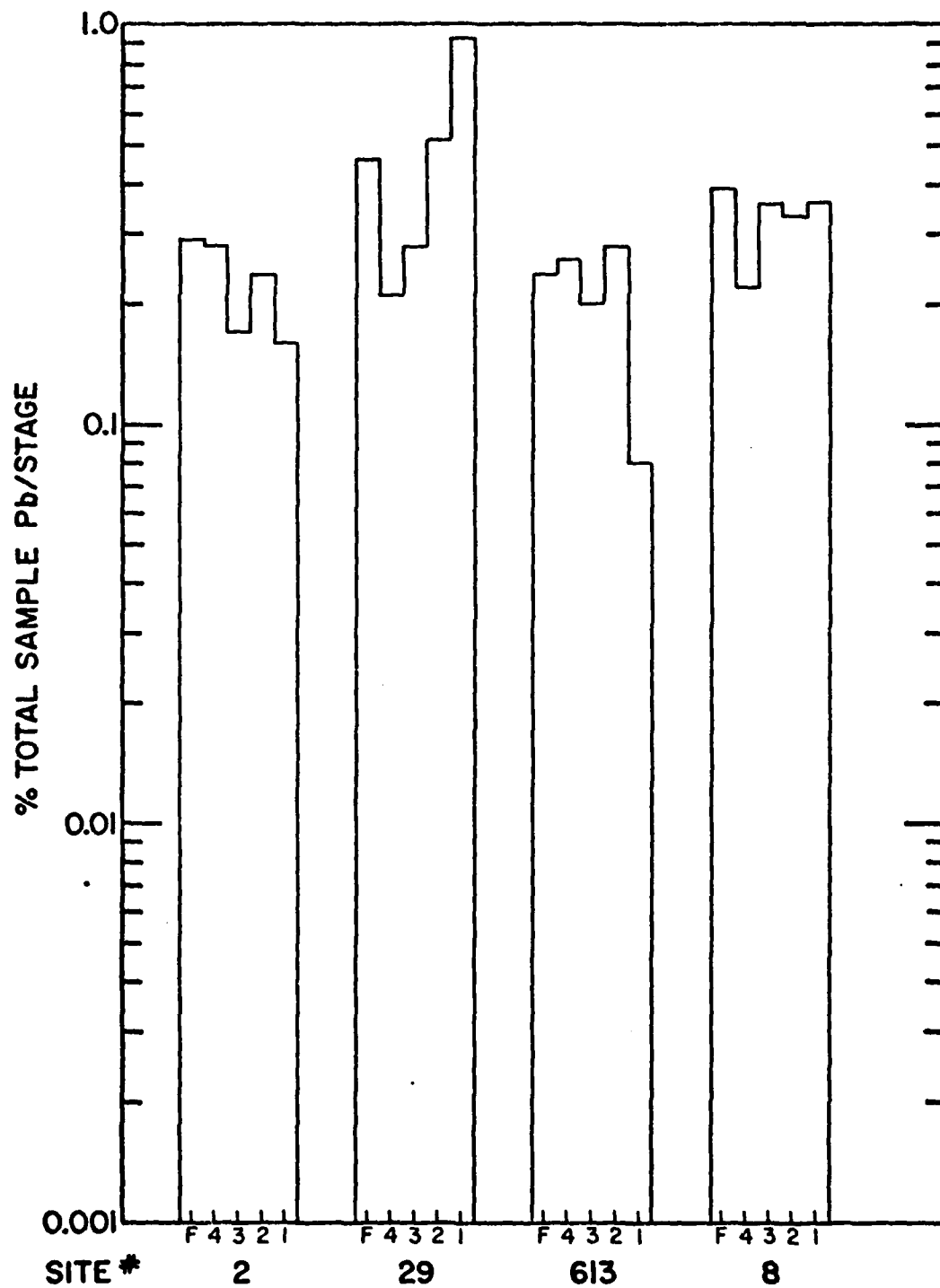
Figure 19. Percent of Total Particulate Collected on Each
Impaction Stage and on Backup Filters as Pb
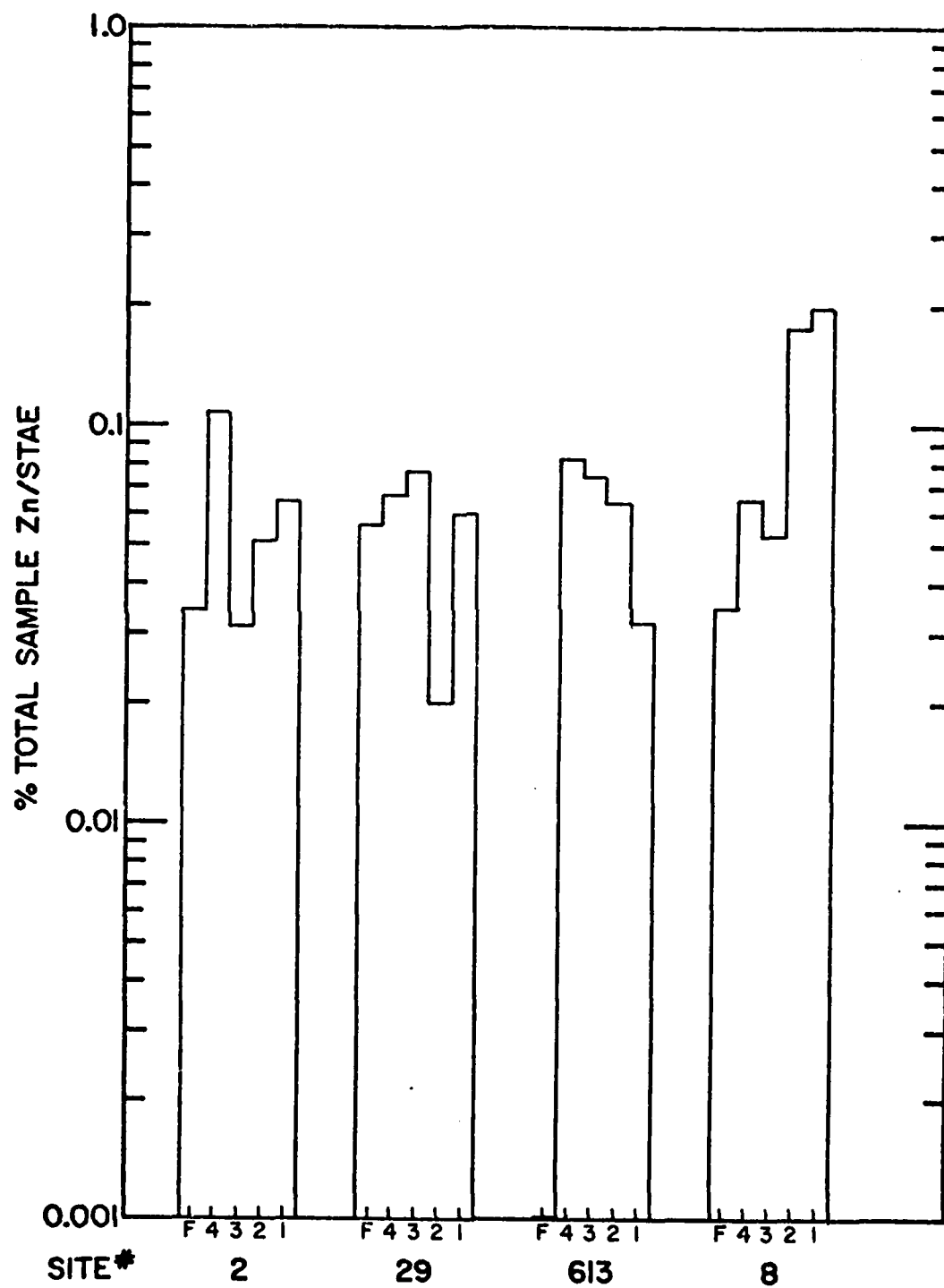
Figure 20.   Percent of Total Particulate Collected on Each
Impaction Stage and on Backup Filters as Zn
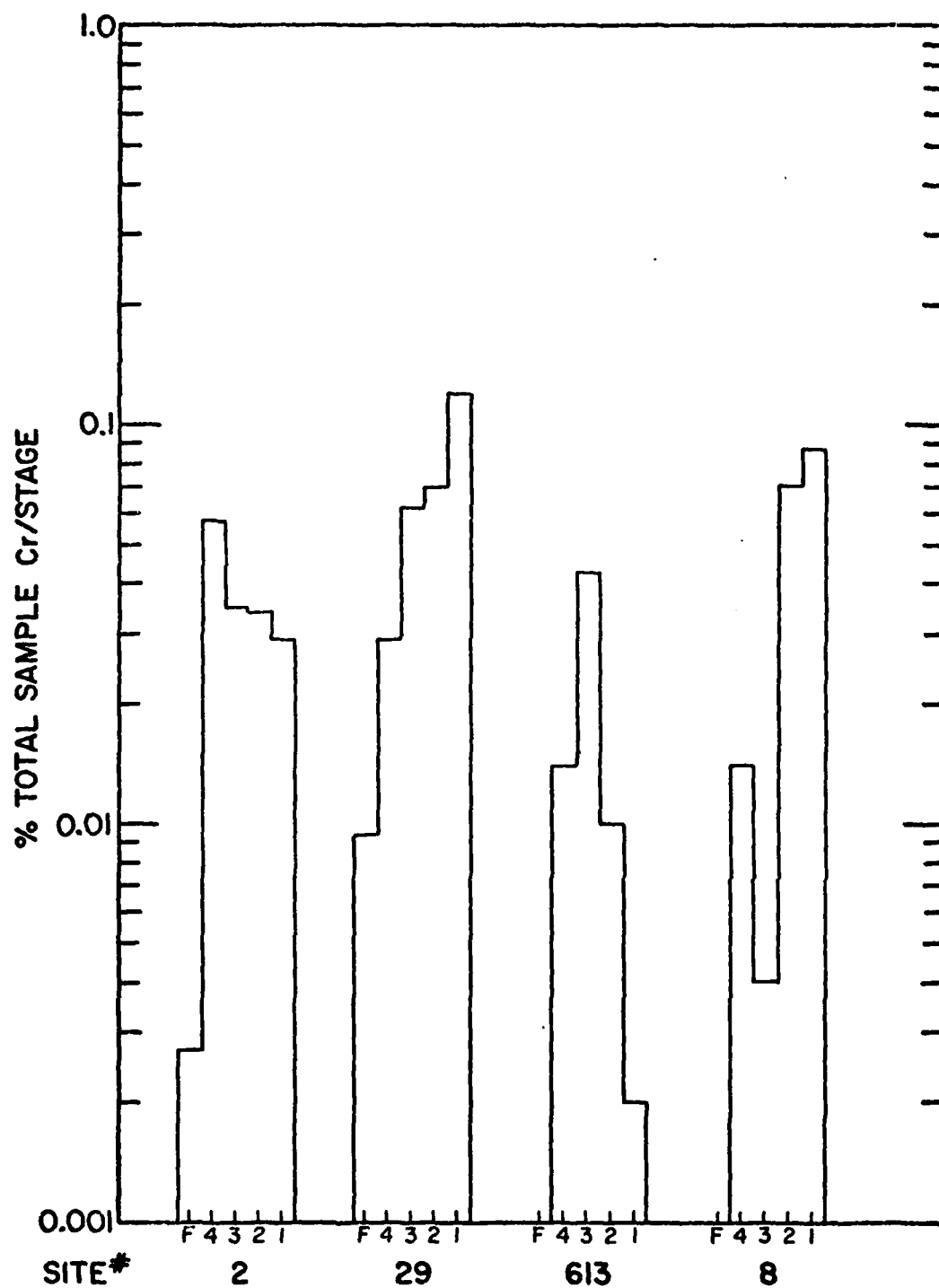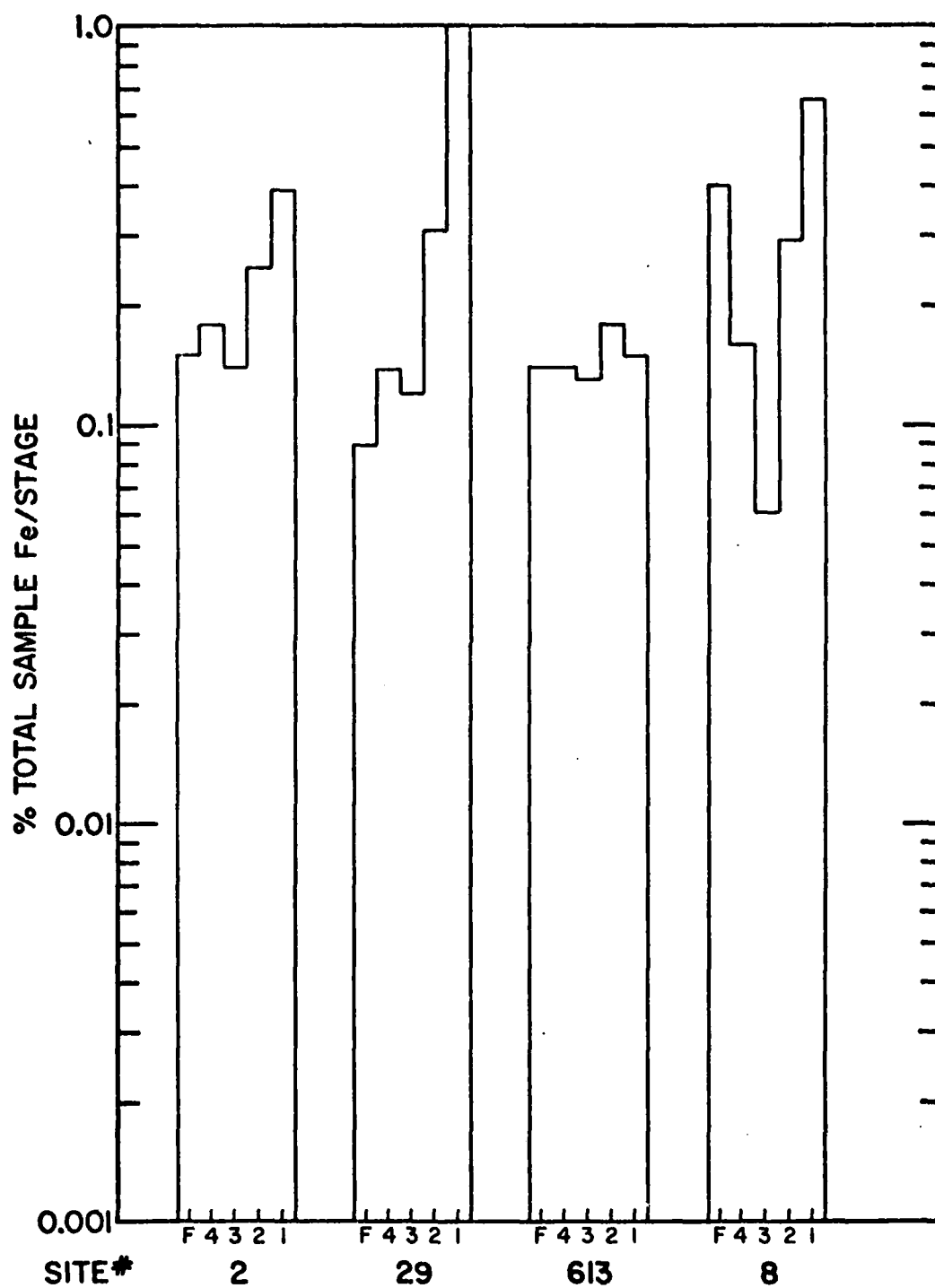
VI. DISCUSSION AND SUMMARY

While generalizations might be made, trends noted, and conclusions drawn from the data presented in this study, it should be borne in mind that these are derived from a single sample at each site. It is anticipated that in a long range study in which winds, weather, emissions factors, and other variables could be correlated to the size distribution and elemental composition of suspended particulate, that the conclusions could be different.

DISCUSSION OF GRAVIMETRIC RESULTS

The operating manual for the Anderson fractionating particulate collector leads one to expect that a major portion of the sample will impinge on the collection disks. However, in this study, 63% to 74% of the total particulate was collected on the backup filters (Table 8). The occurrence of a high percentage of submicron particulate may be due to the formation of secondary pollutants,[17] especially from SO_2 generated by (1) use of high sulfur coal, and (2) from the catalytic converters on late model automobiles. Also, the highly efficient pollution abatement devices currently in use on many point sources, trap nearly all of the larger particulate which probably acted formerly as sites for the aggregation of the finer particles, thereby removing a portion of the submicron fraction from suspension.

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Another consideration peculiar to cascade samplers and, not fully quantified, is the possibility that the force of impaction could cause a conglomerate particle mass to shatter and thereby result in a size distribution skewed to the smaller particle size ranges.

The gravimetric results were plotted on log-probability graphs (figures 7-10) which are the accepted method of presenting particle size distribution data. The resulting curves express the relationship between particle size and cumulative percent (weight) of particulate below a stated particle size. The mass median diameter (MMD) is the particle diameter below which fifty percent of the sample lies. Extrapolation of the log-probability curves in this study revealed MMD's below 0.4 μ. While these MMD's were similar at all four sites, the standard deviations, as calculated by equations (1) and (2), differed significantly. At the urban sites 2, 8, and 29, the values were 10.8 μ, 5.7 μ, and 4.7 μ respectively. At New Carlisle (site 613), which is removed from the industrial particulate fallout, the deviation was 30.1 μ. Since these standard deviations are an indication of the size dispersion of the suspended particulate about the mean, one can conclude that the particle distribution of urban atmospheres is markedly narrower than that found in a more rural type of environment. This is in line with previous investigations which have found that windblown soil, agricultural dusts, and other fugitive emissions are in the size range above one micron, while industrial emissions

generally fall in the one micron and below range.

A previous study[42] has shown excellent agreement between concurrently operated cascade and hi-vol samplers. Therefore, it was not expected that the total suspended particulate levels observed here would be two to three times higher than the previously reported annual geometric means at the sites sampled. This may be a result of a higher collection efficiency with two cellulose paper backup filters as compared to the single glass fiber filter normally used on the hi-vol samplers. Another unquantified variable is the possible difference in the size distribution collected by each sampling method.

The EPA conducted a year long study[21] to determine the feasibility of collecting sized suspended particulate on a routine basis.

Modified Anderson cascade samplers with foil impaction disks and membrane filters were installed in Chicago, Illinois, Washington, D.C., Philadelphia, Pennsylvania, St. Louis, Missouri, Cincinnati, Ohio, and Denver, Colorado. Samples were taken every two weeks and results were averaged for the quarterly and annual periods. The MMD's varied from a high of 2.31 μ for the first quarter in Chicago, to a low of 0.19 μ during the second quarter in Denver. Annual MMD's were above 0.4 μ. Between 54% and 68% of the sample in the EPA study was found in the submicron range. The concentration of the suspended particulate (TSP) ranged between 41.4 μg/m^3 and 97.8 μg/m^3. These lower TSP values, as

compared to the current study, may be due to (1) the use of
a membrane backup filter, (2) the lower sampling rates, (3)
lower SO_2 emissions (the earlier study was done in 1970), a
and (4) the possibly greater overall percentage of particu-
late in the higher size ranges which would settle out of the
air.

DISCUSSION OF ATOMIC ABSORPTION RESULTS

Total Elemental Concentrations. The metals chromium,
iron, manganese, nickel, lead, and zinc present in the sized
particulate samples, were determined by atomic absorption
spectroscopy (Tables 14-19). Nickel, seen in nanogram
amounts and only on the backup filters, was the least abun-
dant of the six elements determined. At the same four sites
sampled in the present investigation, nickel was not detected
by an earlier Brehm Laboratory study.[10] This same study,
however, did show sizeable amounts of nickel (150-300 ppmw)
to be associated with grab samples from a foundry (NIBCO)
and a county incinerator. It is therefore significant that
at site 29, which is northwest of NIBCO, and at site 8,
located south of the county incinerator, that the nickel
levels were at least three times higher than at sites 2 and
613. The nickel concentrations found in this study are lower
than those found in several U. S. cities. In New York City,[12]
levels of 0.01-0.25 $\mu g/m^3$ were reported and the seasonal
increases were associated with the use of fuel oil. Nickel
levels of 0.012-0.017 $\mu g/m^3$ [35] were reported for Elizabeth;

Newark, and Trenton, New Jersey and Bridgeport, Connecticut.
Cincinnati, Ohio,[21] exhibited a reported nickel concentra-
tion of 0.06 $\mu g/m^3$.

As expected, due to the many foundries, large amounts
of iron were seen at all four sites (0.3-0.8 $\mu g/m^3$). These
values are a factor of three to five lower than found by
spark source mass spectroscopy[10] for Dayton, Ohio, but are
comparable to levels detected by atomic absorption,[33] neutron
activation,[15] and emission spectroscopy[21] in other cities.
The highest concentration of iron was detected at site 8, and
the lowest at site 613.

Both in this study and in the earlier Brehm Labora-
tory investigation, the highest concentration of suspended
lead was found at site 29, while the suburban sample, site
613, was the lowest. The lead levels determined in this
investigation were lower than those found in some U. S.
cities,[21,35,36] possibly due to the increased use of unleaded
gasoline. The particulate from site 29 also contained
high Zn, Cr, and Mn compared to the other three sites. Once
again, spark source analysis[10] of grab samples from the
foundry in close proximity to this site were also found to
be high in Cr and Mn. (1000 and 500 ppmw respectively)
Analysis of incinerator ash revealed high Mn (10000 ppmw)
and Zn (1500 ppmw). The Zn and Mn levels at all four
sample sites were comparable to amounts found in a six city
survey conducted by the EPA.[21]

<u>Elemental Size Distributions</u>. Since over 60% of the
suspended particulate in the Dayton metropolitan area was
found to be below 1.1 μ (i.e. collected on the backup fil-
ters) in aerodynamic diameter (Table 8), the elemental size
distribution becomes an important factor in defining air qual-
ity. The distribution of metals is presented by two differ-
ent graphical formats. Figures 11-15 show the fraction of
total metal collected on each stage of the cascade impactor
and on the backup filters. Each fraction can be related to
a specific aerodynamic size range and probable site of deposi-
tion in the human respiratory tract (Figures 4 and 5). Fig-
ures 16-20, charted on 3-cycle semi-log paper, display the
percent of total particulate, collected on each stage of the
cascade impactor and on the backup filters, that can be
attributed to a specific metal. While it might be assumed
that both types of graph would present similar distribution
patterns, this was not found to be true. The reason lies in
the fact that a higher percentage of certain types of par-
ticulate, especially the biological materials, are found in
the larger size ranges thus increasing the total particulate
weights in that particular size fraction but not necessarily
increasing the concentrations of trace metals. Both graphi-
cal formats are meaningful. The distribution of total metal
(Figures 11-15) is important in defining possible sources of
the particular pollutant. A bimodal distribution indicates
two different types of sources; a high percentage within the
larger size ranges points to fugitive emissions, mechanical

processes, windblown soils and the like; while a concentra-
tion in the smaller size ranges indicates origins in stack
emissions. A knowledge of how the metal concentration re-
lates to the total particulate within a given size range
(Figures 16-20) is important in determining potential
health hazards and in designing more effective abatement
devices.

All of the nickel detected in the present study was
collected on the backup filters. Its association with
particles below 1.1 μ and the fact that large amounts of
nickel are seen in foundry dusts and coal[10] points to indus-
trial emissions rather than natural processes as the major
source. Unlike nickel, chromium is distributed over all
five size ranges. As seen by Figure 11, the distributions
show no recognizable pattern from site to site as was found
in a comparison between Cr levels in Cincinnati and its
suburb, Fairfax.[4] It should be pointed out that no Cr was
detected on the backup filters at sites 8 and 613. Approxi-
mately 81% of the Cr was collected on the first and second
impaction stages and only 3% on the third impaction stage
at site 8. Since this site is located in an industrial area,
perhaps the larger fraction results from mechanical processes
and reentrained ash from a nearby incinerator dump. Optical
examination of the particulate at site 8 showed almost no
biological contamination and thus it was not surprising to
see a similarity between the percent distribution of total
Cr and the percent distribution of total particulate as Cr.

(Figures 11 and 16). At site 613, 54% of the Cr was detect-
ed on the third stage of the impactor. This could indicate
a small, localized point source of the metal. Looking at
the total particulate collected, the largest fraction of Cr
at site 613, also falls on the third impaction disk (1.1-
2.0 μ) again indicating perhaps a fugitive emission from a
metal finishing process. Thirty-four percent of the Cr at
site 29 was found on the filters and the remaining amount was
evenly distributed on the impaction disks. At site 2, slight-
ly lower amounts of the metal were found on the filter and
third stage as compared to the other size ranges.

Iron (Figure 12) displays a similar bimodal distribu-
tion at all four sites. As much as 85% of the iron (Site 8)
is found on the backup filters and between 8 and 21% impact-
ed on the upper stage of the cascade sampler. Looking at
Figure 17, iron is fairly evenly distributed throughout the
total particulate sample at the rural site (613), but shows
a definite bimodal tendency at site 8. Over 1% of the total
particulate at site 29 and over .3% at site 2 is iron.

The Mn distribution pattern (Figure 13) is very simi-
lar to iron with large percentages found on the backup fil-
ters and lower amounts detected on the first impaction stage.
A study of sized particulate in Boston, Massachusetts[15] also
revealed a mixed distribution for Mn and Fe. Of interest in
the Mn distribution is the occurrence of the secondary peak
on the second (3.3-7.0 μ) rather than the first (>7.0 μ)
impaction stage at site 8. This reversal also shows up in

Figure 18. It may indicate that there is a minor point source for Mn in the vicinity of site 8 and that this Mn is a fugitive emission from an abrasive type of industrial process. The bimodal distribution at all sites is very evident in the graph of the percentage of total particulate as manganese.

Over 70% of the suspended lead was collected on the backup filters. This compares favorably with findings that 75% and 65% of the lead collected in Cincinnati and Fairfax, Ohio,[4] respectively, was below 1 μ. The major fraction of lead collected in a California study[37] was also less than 1 μ in diameter. It is very significant that lead comprises over 0.1% (Figure 19) of the total particulate collected on any single impaction disk at all of the sites sampled.

The zinc distribution, like those of iron, manganese, and lead, displays a general pattern at the three industrial sites, where at least 49% of the particulate was below 1.1 μ. Unlike the other metals, the distribution at the rural site was noticeably different, which indicates that specific point sources within the industrial environment are emitting small zinc containing particles. Over 50% of the Zn detected in a California[32] study was associated with particles less than 0.5 μ. The latter investigations related this to the incineration of tires and galvanized products. In Boston, Massachusetts,[15] the small size range of zinc containing particles was postulated to arise from industrial processes causing vaporization followed by condensation. Analysis of incinerator ash[10] from Dayton, Ohio revealed zinc levels that were

three to ten times higher (1500 ppmw) than any other indus-
trial or natural source. Surprisingly, Zn was also found in
significant amounts (400-500 ppmw) in street sweepings and
grainery corn dusts.[10]

DISCUSSION OF MICROSCOPIC RESULTS

Since the primary source of heat and electricity in
the Dayton metropolitan area is coal, it was expected that
several of the well characterized morphological classes of
coal fly ash[77] would be readily discerned with the optical
microscope. Particulate indicative of asphalt and cement
manufacturing processes, and foundry operations were also
anticipated to be collected with the cascade impactor. To
aid in identifying these particles, microscope slides were
prepared from grab samples taken at typical local industrial
sites. In addition to those, particles from representative
soils, street sweepings, corn and bean processing, and
municipal incinerator operation were also mounted on micro-
scope slides. These are all documented in photomicrographs
numbered 12 through 32. Slides were also prepared of par-
ticulate collected on each stage of the cascade impactor, but
it was only practical to include herein photos of the par-
ticulate on the first stage at each site. Site 8 contained
such a small amount of sample on the first stage that photos
of the second stage are also included. Table 10 identifies
all of the pictures presented and also shows the resulting
magnification of the sample. At a total magnification of
195 times, one centimeter measured on the photo corresponds

to approximately 51 μ on the actual sample. A total magnification of 390 times is equivalent to 26 μ.

<u>General Observations of Grab Samples</u>. The four soil samples (29-32) are identical when observed optically. They are approximately 90% anisotropic (have more than one retractive index) and consist of quartz minerals, shale, iron oxide and clay. The coal fly ash particles (20 and 21) are principally spherical in shape and can be hollow, solid, or filled with smaller spheres. Also, pieces of partially burnt coal, resembling black swiss cheese, are seen. The irregular coal particles (11) are black in transmitted light. The road sample from American Aggregates (14) consists mostly of irregularly shaped anisotropic calcite and assorted silicates. The Armco sample (13) is a mixture of cement, fine limestone and rough surfaced spherical particles resembling fly ash. The Dura-Crete (15) sample was mostly limestone. The Northwood asphalt hopper sample (12) is a mixture of silicates. The shotblast from NIBCO (18) consists of a few particles of casting sand, iron oxides and some black iron particles, while in contrast the sand handling system is almost completely large black iron particles with some spent casting sand, calcite and silicates. Photo 23 shows cement particles from South West Portland Cement and photo (24) is the same except that the particles are more rounded. The very fine particulate from the alkaline bypass is limestone (25). The starch particles in photos 16 and 17 are easily recognized by their ovoid to ellipsoid shape and central air bubble

which shows up as a dark spot in the center of each particle.
Under polarized light, a characteristic interference pattern
in the form of a black cross appears on each particle. The
street sweepings (27, 28) are mostly soil, sprinkled with
wood fibers, asphalt, iron oxides, fly ash, and some biolog-
ical materials. The incinerator ash (21) is the most inter-
esting and contains a variety of substances, large dark
pieces of partially burnt wood fiber, some residual anisotrop-
ic crystalline materials and isotropic, translucent particles
of fused ash. The sample also contained a profusion of
unidentifiable isotropic needle-like particulate.

Particulate Collected in Dayton, Ohio. The airborne
particulate can be classified generally as biological or
industrial on the basis of microscopic analysis. The biologi-
cal dusts include pollen, spores, insect parts, fungi,
diatoms, moth and butterfly scales, wood fibers and the
like. Industrial dusts include such things as fly ash, coal,
coke, glass-fiber, corundum, catalysts, cements, natural
and synthetic fibers, starch, iron oxide, limestone, quartz,
sand, and asphalt. Many of these particles were observed on
the actual cascade impactor disks.

Photomicrographs 1 and 2 are of the particulate
collected on the first stage of the impactor at Site 2.
Approximately 15% of the sample consists of biological mat-
erials, various pollens, insect scales and fungi conidia.
The rest of the sample includes wood fibers, soil particles

and many fine black particles. Of particular interest are the fly ash spheres (0.1 μ), highly visible at the 390x magnification. The particles range in size from below 0.1 μ to approximately 30 μ.

A sample of the particulate collected at site 29 is seen in photos 3 and 4. Biological materials constitute a slightly larger fraction of the total particulate at this site. Particularly notable are the spider-like spore (3) and the fungi fragment (4). Silver maple trichomes and starch particles were also observed. Inorganic materials included calcite, glass fibers and fly ash. Particles ranged in size from lengths of over 100 μ to the ultra-fine barely visible.

A preponderance of fungi conidia was seen in the sample collected at site 613.[5-7] In fact, over 40% of the sample seemed to be biological in origin. It is significant to note that this sample contained very few fly ash type particles and the inorganics were mostly windblown soil and irregular shaped black particles.

At site 8, almost no biological material was collected, in fact, there were few particles seen on the first impaction disk at all (8,9) and these were predominately pieces of coke, fly ash and iron oxide. Examination of the particulate on the second impaction stage (10,11) once again revealed few biological materials, many fly ash particles and a number of red iron oxide particles. Besides the abundance of iron oxide collected at this site, the narrow range of

particle diameters deposited on each impaction stage is noteworthy.

SUMMARY

A four-staged Anderson Cascade impactor has been used to collect 24-hour sized particulate samples of suspended particulate at four sites in the Dayton, Ohio metropolitan area. The size to weight distributions of the particulate were plotted on log-probability paper. The extrapolated mass median diameters (MMD) were found to be below 0.4 μ and fall within the range of values reported in other cities. The standard deviation of the MMD at site 613 was significantly larger than at the industrial sites indicating a more highly dispersed particle distribution at the rural site. Six elements, Cr, Fe, Mn, Ni, Pb, and Zn were identified in the size fractionated particulate by atomic absorption spectroscopy. Nickel was the least abundant occurring in nanogram amounts in the smallest size fraction. Iron, manganese, and zinc have bimodal size distributions which are skewed to the lower particle size ranges. In fact, over 60% of the total metals analyzed is associated with particulate which may be retained by the lung. The Cr distribution has no overall site to site pattern suggesting, perhaps, small localized point sources rather than major industrial contamination. The elemental concentrations determined in this study compared favorably with values found in an earlier study of the suspended particulate matter in Dayton and were within the

range of values found in other U. S. cities. Correlations
can be made with winds, point sources, and elemental concen-
trations at the sampling sites.

The microscopic examination of the impacted particu-
late revealed many particles which could be identified by
comparison with particles from known industrial sources.

Several observations concerning the characterization
of airborne particulate as it relates to elemental size dis-
tributions and optical identification have been made in
this study. However, because the data is based on only a
single sample at each of the four sites, it should be
recognized that a long term study in which the variations
due to winds, weather and seasonal fluctuations would aver-
age out, could yield results different from those presented
here. The specific merits of this thesis research are that:
(1) it affirms the need for further particulate characteriza-
tion; (2) it suggests that elemental analysis of sized
particulate yields data pertinent to the identification of
possible particulate sources; (3) it identified the signifi-
cant impact of point sources on the increasing particulate
levels seen in Dayton, Ohio, and (4) it shows that optical
microscopy can be a practical supplementary tool for
particle characterization.

The results of this study indicate that a major fraction
of the particulate falls well within the size range of
probable deposition in the human respiratory tract and is
likely generated by industrial processes. Thus, it is felt

that a long range investigation of sized suspended particulate which considers variables such as wind speed and direction, rainfall, point source emissions factors and atmospheric sulfates would provide critical information necessary to a full understanding of the particulate problem in the Dayton, Ohio metropolitan area.

APPENDIX A

AMBIENT AIR QUALITY STANDARDS
SUSPENDED PARTICULATE

Ohio	Federal	
60 μg/m^3	a 75 μg/m^3 b 60 μg/m^3	maximum annual geometric mean at any sampling site
150 μg/m^3	a 260 μg/m^3 b 150 μg/m^3	maximum 24-hour concentration not to be exceeded more than one day per year

[a]primary standard -- defines levels of air quality necessary to protect public health

[b]secondary standard -- defines levels of air quality necessary to protect public welfare from any known or anticipated adverse effects of a pollutant

APPENDIX B

SUSPENDED PARTICULATE
ANNUAL GEOMETRIC MEAN AT SAMPLE SITES

(Ref: Air Quality Reports
1973-1977)

YEARS
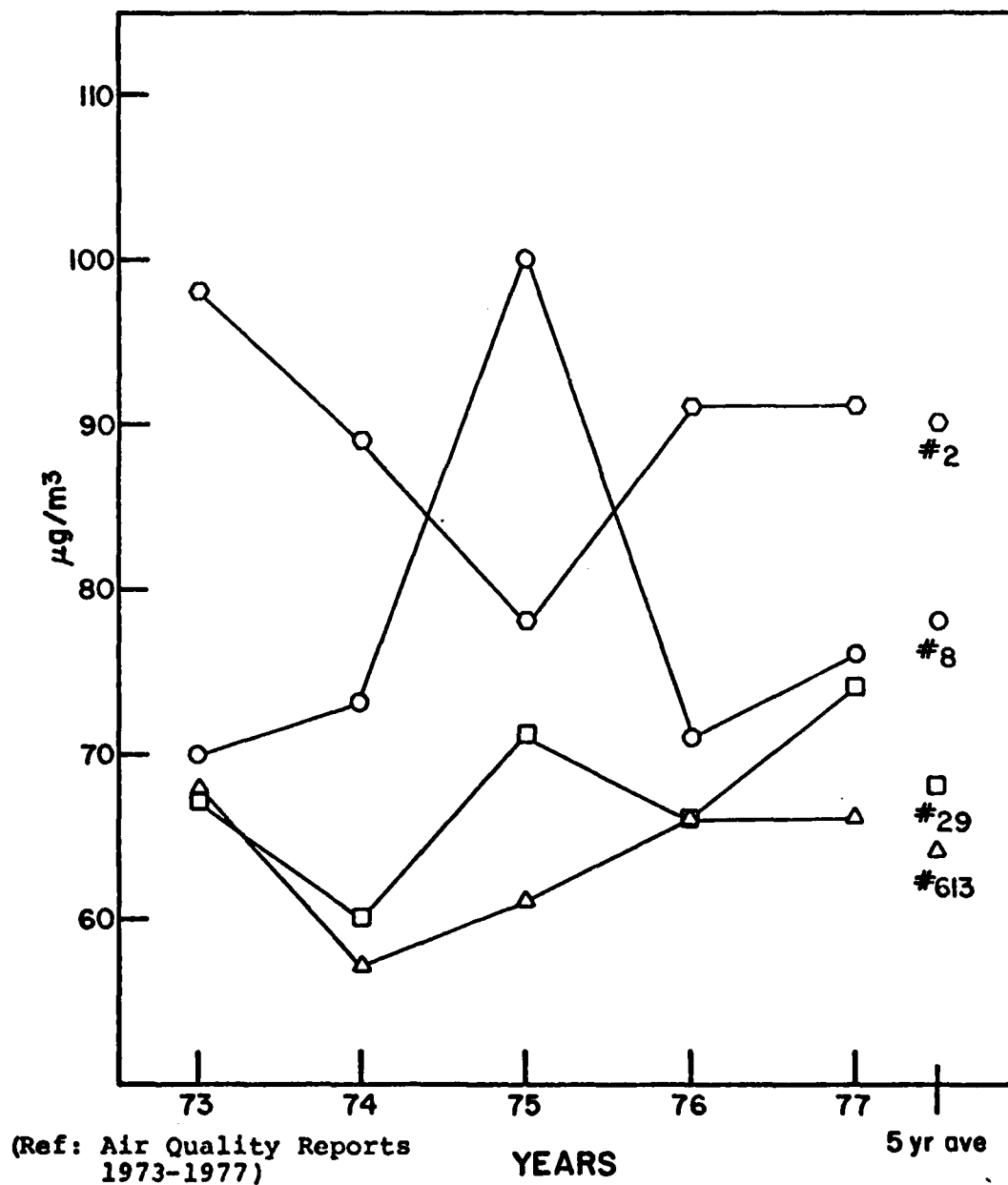
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VITA

After completing her B.A. in Chemistry at Rivier College in Nashua, New Hampshire, Captain Lorelei Krebs received her commission as a second lieutenant in the U. S. Air Force. She was assigned, as an analytical chemist, to the Air Force Rocket Propulsion Laboratory at Edwards Air Force Base, California, where she worked with rocket propellants and jet fuels. In January of 1976, after being restationed at the Air Force Radiological Health Laboratory at Wright-Patterson AFB, Dayton, Ohio, she enrolled as a part-time graduate student at Wright State University. She was reassigned to the Air Force Institute of Technology in September, 1977, and was allowed to pursue her graduate studies as a full-time WSU student completing all degree requirements in December, 1978. Her projected assignment is with the USAF Office of Scientific Research, Directorate of Chemistry, Bolling AFB, Washington, D.C.

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